Process Design, Simulation and Optimization of Acrolein Production from Bioglycerol

Undergraduate Thesis

Yury Andrea Castañeda López
Cód. 201210034004

Advisor: Santiago Builes, Ph.D
Co-Advisor: Diego Acosta, Ph.D

EAFIT University
Engineering School
Department of Process Engineering
Medellín, Colombia

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1. Introduction

1.1. Crude glycerol valorization

Due to globalization, the chemical industry has increased consumption of fossil resources to meet the needs of the rising demand, correlated to world population [1]. Therefore, greenhouse gases and pollutants emissions have increased continuously. It is necessary therefore to produce energy and substances from renewable resources. This will allow to reduce emissions and to decrease dependence on non-renewable resources. Much attention has being paid to replacing fossil fuels and reduce carbon dioxide emissions by using renewable fuels such as bioethanol and biodiesel, for the production of energy and chemicals [2].

Bioethanol can be produced by fermentation of sugars, starch crop or lignocellulosic biomass, which includes agricultural residues, herbaceous crops, forestry wastes, wastepaper, and other residues [3]. The energy content of ethanol is higher than the energy required to produce ethanol [4-5]. Thus, it has the potential to be a sustainable transportation fuel, as well as a fuel oxygenate that can replace gasoline [3]. Biodiesel is a diesel fuel made from renewable sources such as vegetable oils and animal fats by transesterification with alcohols [6]. Its production generates approximately 10% by volume of glycerol as a by-product. Glycerol obtained from transesterification of oils has several impurities that need to be removed by different separation processes to produce pure glycerol [7]. Crude glycerol costs US $150 /metric ton [8] whereas pure glycerol costs US $600/metric ton [9].

Different processes have been proposed for valorization of bioglycerol for instance:

- Hydrogenolysis of glycerol to produce propane diols [10] such as 1,3 propanediol, which is a simple organic chemical with a wide variety of applications in polymers, foods, cosmetics, lubricants and medicines [11].
- Polymerization of glycerol to obtain diglycerol (DG), which is a useful compound for food, cosmetic and chemical applications [12].
- Etherification of glycerol to produce ethers, in particular, *tert*-butyl ether which is considered promising as an oxygenated additive for diesel fuels[13]
- Steam reforming, partial oxidation or auto- thermal reforming of glycerol to produce fuels as hydrogen [11].
- Acetylation of glycerol to produce esters [14].
- Dehydration of glycerol to produce specialty chemicals, like acrolein; precursors of materials, such as polyesters and polyethers [11].

In Colombia different research groups have studied valorization of bioglycerol to produce different chemical products, such as methyl esters [15], ethanol [16], poly-3-hydroxybutyrate [17].

Acrolein is produced industrially by the oxidation of petroleum-derived propylene with a Bi/Mo-mixed oxide catalyst at 300–450 °C [18]. However, acrolein can also be produced by catalytic dehydration (heterogeneous or homogeneous) of glycerol at high temperatures. In this process glycerol loses water to produce acrolein. Different processes have been proposed for dehydration of bioglycerol: dehydration in the presence of a catalyst [7], gas-phase dehydration with heteropoly salts as catalysts [19], dehydration in sub and supercritical water conditions [18] and low-pressure packed-bed gas-phase dehydration [20]. In this work, the dehydration in presence of a porous solid catalyst will be considered for the simulation and design of the acrolein production plant. A heterogeneous catalysis will be chosen due to the feasibility to separate the catalyst from reaction mixture in a straightforward manner by physical methods and a higher selectivity in comparison to a homogeneous catalysis [10].

1.2. Acrolein from crude glycerol

In order to produce commercial acrolein from crude glycerol, glycerol purification and dehydration steps are required. The latter consists of two main operations: reaction and purification. This, involves a series of separation processes to obtain highly pure acrolein. A sketch of the simplified process diagram is shown below (Figure 1).

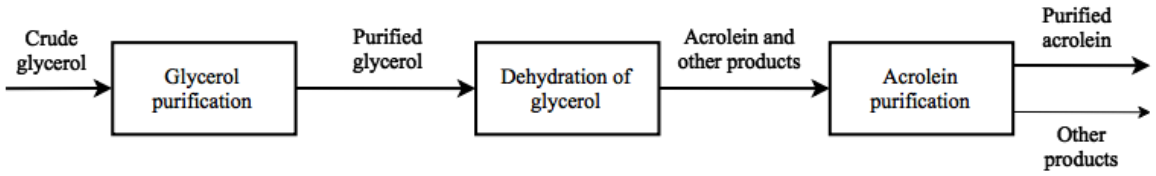
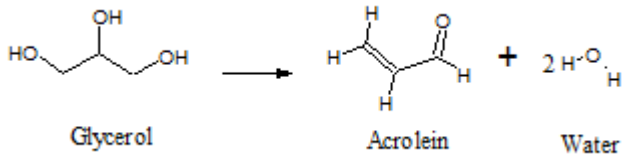


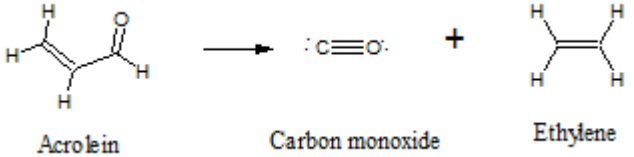
Figure 1. Simplified diagram of acrolein production process

The first step of the process is the purification of crude glycerol because it contains a series of remnant impurities from biodiesel production, such as water, ashes, soap, methanol and salts. Each one of these impurities requires a specific unit operation for its removal. Ashes can be separated by filtration, salts are removed employing membranes, methanol is separated by distillation and soap particles are removed by addition of a flocculant [7].

The dehydration section to produce acrolein consists of a packed bed reactor with a zeolite MFI as catalyst industrially available from BASF or ACS Material [21]. The main reactions that occur in the process are:



(1)



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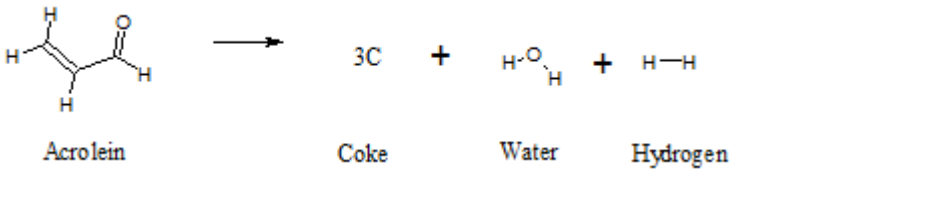

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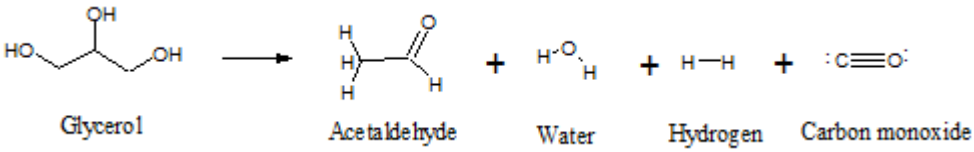


(4)

In reaction 1, glycerol dehydrates, to produce Acrolein (C_3H_4O) and water. Undesirable products such as: hydrogen, carbon monoxide, ethylene, water and acetaldehyde are also produced (reactions 2-4). Therefore, further purification and separation steps are required to obtain the final products. A general representation of this process is shown in Figure 2.

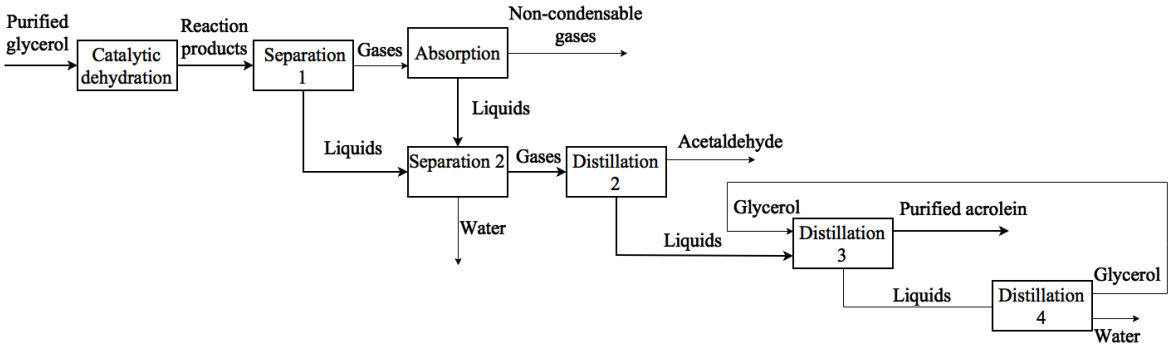


Figure 2. Acrolein production process

Usually, the first separation unit is an absorption column used to separate hydrogen, carbon monoxide and hydrocarbon gases from the liquid phase and a reboiler absorption column eliminated water content. Then, a distillation column is used to separate acetaldehyde from the heavier liquids. A second distillation column is used to separate an aqueous solution of acrolein using glycerol as entrainer. Refined acrolein is obtained on the distillate and a glycerol solution is obtained at the bottoms, which are connected to a third distillation column in order to split water and glycerol and recycle the latter to the second distillation column [7].

In this process besides acrolein as a main product, acetaldehyde is also obtained. Acetaldehyde at high purity is obtained at the first distillation column. Acetaldehyde is produced industrially by oxidation of ethylene [22]. It is a feedstock used in the production of perfumes, polyester resins, basic dyes, solvents for different industries (rubber, tanning, and paper), preservatives for fruits and fishes, flavoring agents, gelatin hardeners and denaturants for alcohol [23]. The global market for acetaldehyde has been trending downward for the past twenty years as a result of the commercialization of more efficient technologies to synthesize products formerly based on acetaldehyde [24]. In 2012, the global production for acetaldehyde was 1,3 MM tons [25].

High purity acrolein obtained from the second distillation column is the simplest unsaturated aldehyde. It has high synthetic and technical potential due to the conjugation of the carbonyl group with a vinyl group. Acrolein is employed as biocide due to its antimicrobial activity and refined acrolein is mainly used for the production of methionine [1].

1.3. Catalysts to improve acrolein production

The conversion of glycerol to acrolein requires the use of a solid catalyst. Several catalysts have been used, with different conversions of glycerol and selectivity towards acrolein. Markočič et al. [26] decomposed glycerol at super critical conditions in the gas-phase in presence of a heteropoly catalyst, mainly alkali compounds, to obtain chemical intermediates, mainly acrolein. They showed that the conversion for dilute feed solutions of glycerol in supercritical water increased with temperature and reaction time. The pressure and the initial concentration of glycerol increased the yield of acrolein using the heteropoly catalyst until the decomposition reaction (Equations 2 and 3) where acrolein decreased in absence of glycerol. Alhanash et al. [19] studied glycerol conversion to acrolein using Caesium 12-tungstophosphate (CsPW) as catalyst. The reaction products consisted mainly of acrolein. They showed that CsPW is an active catalyst for the dehydration of glycerol to acrolein, with a glycerol conversion of 100% and acrolein selectivity of 98%. However, the catalytic activity decreased significantly with reaction time. Corma and collaborators [27] produced acrolein from gas-phase glycerol/water mixtures with zeolite MFI. They showed that dehydration of glycerol at 350 °C on a zeolite-based catalyst in a moving-bed reactor can be used to produce acrolein and other oxygenated chemicals, such as acetaldehyde and acetone. Cecilia et al. [28] showed that the dehydration of glycerol can be activated in presence of vanadium doped mesoporous SBA-15 to produce acrolein at 325°C after 2 h with 80-93% of glycerol conversion and acrolein yield of 26%. Dalil et al. [29] obtained 73% of acrolein selectivity after 6 h on steam from dehydration of glycerol in presence of WO_3/TiO_2 at 280°C. They reported that acrolein selectivity increased with an increase in coke formation. HSiW supported on Al_2O_3 was used as a catalyst by Lui et al [30] Acrolein selectivity was 75% at 300°C after 2 h on steam. Yan and Supples [31] studied low pressure packed-bed gas-phase dehydration of glycerol in presence of H_3PO_4/activated carbon and various solid acid catalysts prepared by wet impregnation of commercial α-Al_2O_3. They showed that acrolein selectivity was 84% at 260°C and 0,85 bar. Zhang et al. [32] dehydrated glycerol on MFI based zeolites using various MFI zeolites with different Si/Al ratios; the optimal conditions were found for Si/Al ratios between 34-38 with a glycerol conversion of 100% and acrolein selectivity of 86% after 2h.

The use of solid catalysts improves acrolein selectivity and conversion for the dehydration of glycerol. Moreover, the product distribution can change dramatically depending on the choice of catalyst. The different catalysts studied offer many possibilities to obtain high yields. In particular, zeolite MFI due to its large surface area and sufficient acid sites, [27] (i.e. the active site for the conversion of glycerol), minimizes the production of acetaldehyde and maximizes the production of acrolein [27,32]. In this work zeolite MFI is chosen as the catalyst for the dehydration reactions of glycerol. In Table A3 are shown the physico-chemical characteristics of MFI used for the conceptual design and simulations.

1.4. Acrolein market

Approximately 350.000 ton of acrolein are produced annually worldwide, mainly in USA, China, Japan and EU [33-34]. The main uses of acrolein are:

- An intermediate for the synthesis of both acylic and acrylic acid esters [11]
- As a slimicide in the manufacture of paper [11]
- As a biocide for controlling microorganisms in water used in oil fracking and production systems [35].
- As feedstock, for treatment of fibers and production of chemicals, like acrylic acid, esters and medicines.
- Growth control agent of microbes in food process lines due to its antimicrobial activity [36].

Acrolein is rarely sold as a commodity in large amounts in the open market. This product is often used immediately after synthesis for the manufacture of other chemicals due to its instability and safety hazards [37]. Nevertheless, it is also possible to use hydroquinone to stabilize acrolein [38], therefore the packing and labelling are important things to considered in the economic analysis; however, there were not taking into account due to those data do not modified the optimization of the acrolein production process proposed in this project.

Although Colombia, does not manufacture acrolein, from January 2016 to May 2016 Firmenich S.A and Colorquímica S.A conducted fifty eight transactions related to the purchase of 200 ton of acrolein or products obtained from it [39].

In 2015, 600 million liters of biodiesel were produced in Colombia [40] where for every liter of biodiesel produced, 0,1 L of glycerol is produced.

1.5. Design of an acrolein process

Posada Duque [36] proposed a conceptual design and simulation of a plant for acrolein production using H_2SO_4 as a homogeneous catalyst. The dehydrogenation reaction took place at 275°C and 1 bar. This work considered the acrolein purification after the reaction to obtain an acrolein stream with 98,5 wt.%. However, this operational requirement increased the overall manufacture costs. Subsequently Posada et al. [41] studied the conversion of raw glycerol to nine value-added products including acrolein, using both crude (88 wt.%) and USP (98 wt.%) grade glycerol. The former required a further refining process using an ion exchange resin, which removed the triglycerides contained in the mixture. Dehydration of glycerol to acrolein as an acid catalyzed process was considered using the reaction scheme reported by Tsukuda et al.[42] in presence of Silicotungstic acid supported on silica with mesopores of 10 nm. They reported a conversion of 100% and molar yield for acrolein of 85,2%.

Conversion of crude glycerol to value added products can reduce the cost of biodiesel production and benefit the biodiesel industry. The main goal of this work is to report and to evaluate the production of acrolein from crude glycerol in a dehydration plant in Colombia using MFI as catalyst. This work will contribute to the development of applied research in renewable energies. This project will also allow the estimation of optimal process conditions

for the base case in order to (i) reduce the waste generation, (ii) increase the acrolein production as the desirable product and (iii) improve the economic indicators with respect to the base case. The economic viability of a crude glycerol dehydration plant located in Colombia and acrolein production will be assessed, considering the impacts on the biodiesel industry and society in general. To the best of our knowledge, a study of this kind has not been pursued before.

2. Methodology

2.1. Project Design Specification (PDS)

The physicochemical properties of glycerol [9], MFI zeolite [38] and acrolein [43], required to design the process were obtained from the literature. Information such as: transport regulations; UN recommendations for transportation of dangerous goods; acrolein and acetaldehyde market; raw materials availability; applicable laws and health; and hazard information, were determined in order to identify critical economic conditions, environmental restrictions and plant location. The market analysis takes into account national and international consumption of acrolein and acetaldehyde [24, 34] trade indicators [44] and import and export data [45-46]; for further details see Appendix A.

The plant capacity was calculated taking into account crude glycerol availability in Colombia (Santa Marta, Barrancabermeja and Meta) [47]. The biodiesel annual production in Colombia is 600 million L [40] therefore, the crude glycerol annual production is 60 million L which corresponds approximately to 57.000.000 kg/year of glycerol.

2.2. Conceptual Design Package

The conceptual design package includes the process mass balances and their corresponding diagrams (In-Out diagram, B.F.D. and P.F.D.), the equipment design and the resulting equipment data-sheets and the financial analysis. For further details of the conceptual design package see Turton [48].

The global inputs and outputs, the reaction equations, and the inputs and outputs of every equipment obtained from the process mass balances were used for the constitution of the In-Out diagram and the Block Flow Diagram (B.F.D.). The control loops were designed considering the operating conditions of each equipment, and the physicochemical information of each stream. The Process Flow Diagram (P.F.D.) was built according to ISO 10628 standard [49]. The sizing of the equipment involved in the process was done according to heuristics from Walas [50] and the equipment were design using properties and conditions of the input and output streams obtained from the simulations in Aspen HYSYS.

The equipment required for saponification of fats and neutralization of glycerol are chemical reactors. However, for simplicity in the calculations, they were considered as agitated vessels, given that the glycerol purification is a batch process [51].

The design of the distillation columns to purify the products of glycerol dehydration was performed using a model based on Underwood-Fenske and Gilliland with an algorithm

reported by Biegler et al. [51]. The information involving the equipment design is summarized in the equipment data-sheets using the format suggested by Walas [52] and is shown in Appendix C.

In the economic analysis the Fixed Capital Investment (FCI), Cost of Operating Labor (C_{OL}), Cost of Utilities (C_{UT}), Cost of Waste Treatment (C_{WT}), Cost of Raw Materials (C_{RM}) and the Cost of Manufacturing (C_{OM}) are performed and calculated using the CEPCI Index from 2011 and updated to 2015 [48]. The profitability of the project was determined using the Internal Rate of Return (IRR) and the Net Present Value (NPV).

2.3. Simulation

Aspen HYSYS V8.4 [53] was used to simulate the production process. The fluid package with the best fits for all the streams was *extended NRTL* for the liquid phase and *Peng Robinson* (PR) for the vapor phase. It is an appropriate model for chemical systems that have different boiling points and when vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) take place. The binary coefficients for both models were estimated using UNIFAC VLE and UNIFAC LLE, respectively. Simulation results from Aspen HYSYS were validated using case studies comparing them to experimental data from literature [54-56].

The glycerol purification process was simulated using mass balances in order to identify how to remove the crude glycerol impurities. It is important to note that for this stage, the simulations did not take into account rigorous reactions. The reactors, decanter and filter were defined as components splitters. The separation steps were specified with the mass balances. Saponification was carried out in a reactor (C-1) to remove the esters and the output stream was separated by a decanter (F-1) in order to split the organics and the glycerol phase, which was fed in a reactor (C-2) to neutralize the salts and favor their removal by filtration (F-2). Then, the filtrate without salts was fed to a distillation column (K-1) to separate glycerol from methanol and obtain purified glycerol. The simulation scheme of the process is shown in Figure 3.

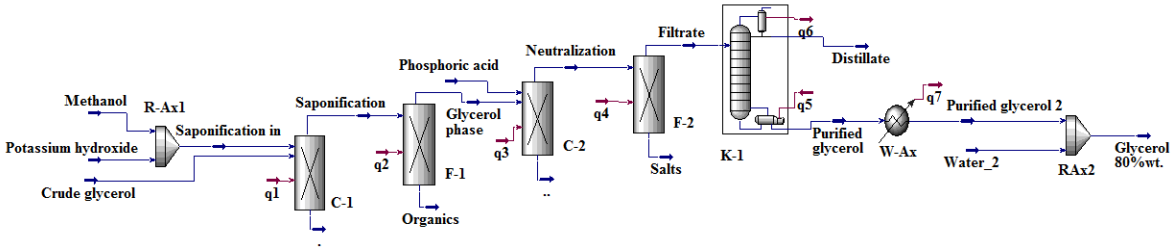


Figure 3. Base case design of the glycerol purification implemented in Aspen HYSYS

To simulate the glycerol dehydration process, a kinetic type reaction was employed because it does not take into account the mass transfer velocity between the components and the catalyst. The kinetic parameters, that is, the exponential factor A_i and the activation energy E_i, are those of the Arrhenius equation as shown in equation 5 and Table 1.

$$K_i = A_i \exp(-E_i/RT) \quad (5)$$

Table 1. Kinetic parameters of glycerol dehydration reactions [7]

Parameter / Chemical reaction	Ai (kgmol/kgcat s)	Ei (kJ/kmol)
Equation 1	$1{,}05 \times 10^{4}$	$2{,}7 \times 10^{4}$
Equation 2	$6{,}31 \times 10^{4}$	$6{,}62 \times 10^{4}$
Equation 3	$1{,}92 \times 10^{2}$	$1{,}05 \times 10^{4}$
Equation 4	$3{,}75 \times 10^{4}$	$3{,}79 \times 10^{4}$

The kinetic parameters were estimated using partial pressure, the catalytic density and its void fraction. These parameters were converted to Aspen HYSYS format using the void fraction (0,75) and the catalyst density (720 kg/m^3). This allowed the conversion of the reaction rate in terms of weight of the catalyst to volume of the reactor. Reaction 3 was not considered in the simulation of the system because the produced carbon is a solid that can be removed from the process before catalyst deactivation occurs.

Glycerol dehydration consists of two main operations: (i) reaction and (ii) purification. The latter involves a series of separation processes in order to obtain acrolein with a high purity. The reaction takes place in a plug flow reactor (C-3) and the gas-phase output stream is compressed with a compressor (V-1) and then cooled (W-4) in order to separate the non-condensable gases using a separator (K-2) and an absorption column (F-3). The liquid stream is then fed in a reboiler absorption column (K-3) to eliminate as much water as possible. Then a distillation column (K-4) is used to separate light compounds (acetaldehyde). Subsequently, an azeotropic extractive distillation was performed (K-5) adding glycerol as the solvent that breaks the acrolein-water azeotrope, in this step it was necessary to add a sub-flowsheet to carry out the LLE separation. Finally, a distillation column (K-6) was employed to separate glycerol and water, to recycle glycerol to the azeotropic distillation column. The adjust function was used to avoid glycerol losses in the process. The pressure losses were not taken into account through the process. It is important to note that shortcut columns were simulated previously to determine the column trays. A sketch of the process is shown in Figure 4.

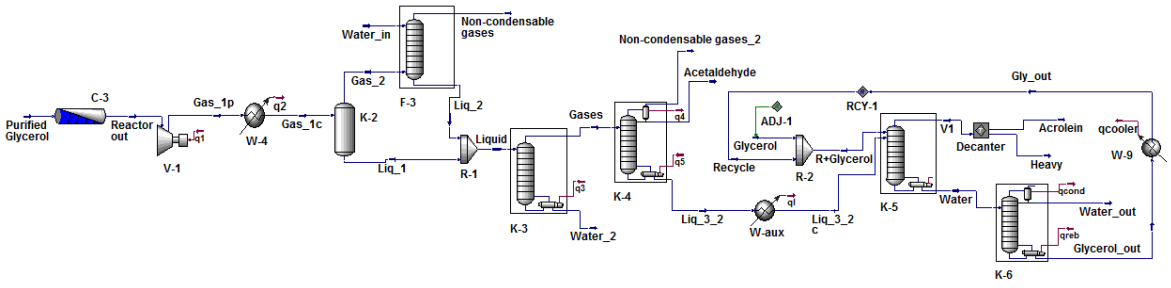


Figure 4. Base case design of the acrolein production implemented in Aspen HYSYS

Azeotropic distillation of acrolein water employs extractive distillation [57]. In azeotropic distillation a heavy entrainer (glycerol in this case) is used to separate a mixture exhibiting a minimum boiling point azeotrope, the entrainer has a higher boiling point (290°C for glycerol) than the pure components (53°C and 100°C for acrolein and water, respectively) at standard conditions. Glycerol does not form any azeotropes with either of the pure components water and acrolein. Thus, a residue curve map was built using NRTL as the fluid package with CHEMCAD software [58], in order to see the vapor-liquid-liquid behavior and verify that the addition of glycerol does not form azeotropes. Figure 5, shows the ternary diagram which exhibits topological consistency because the curve starts at the binary azeotrope and ends at acrolein edge of the composition triangle, which means that acrolein is part of the distillate from the extractive column (K-5) and the component recovered as the extractive column (water) could be distillate from the entrainer recovery column (K-6). At the same time, there are not distillation boundaries that divide the composition space into two distillation regions which indicates that glycerol is a feasible entrainer to separate acrolein from water.

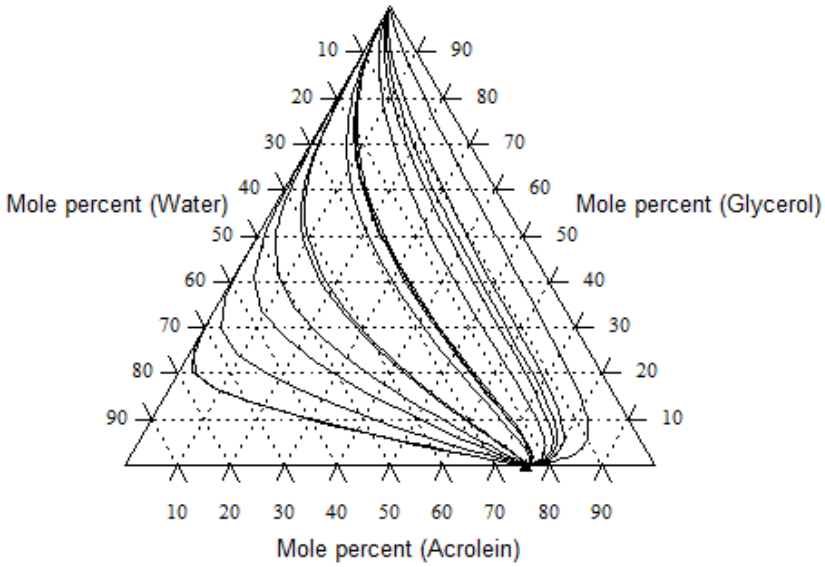


Figure 5. Residue curve map for Water/Glycerol/Acrolein. Residue curve at 11,01 bar, bimodal plot at 80°C. Acrolein = 141,2 °C, water = 179,5 °C and glycerol = 400°C. Binary azeotrope (acrolein, water) = (75,5%-24,4%) at 134,7 °C and 11,01 bar.

2.4. Process Optimization

The model simulated in the previous section was established as the base case for optimization. The acrolein selectivity and the losses after purification were analyzed in order to improve the quality of acrolein expressed in terms of mass flow and mass fraction. Moreover, some variables were considered as susceptible to be optimized, such as:

i. Reactor length: In order to improve the acrolein selectivity, the reactor length effect on the products distribution was studied up to 10 m.

The acrolein selectivity was calculated using the equation reported below [59]. However, it is important to note that it was not possible to obtain a selectivity of 1 because of this

selectivity definition, therefore, it was intended to obtained a high selectivity as were possible.

$$Selectivity = \frac{Exit\ molar\ flow\ rate\ of\ desired\ product}{Exit\ molar\ flow\ rate\ of\ undesired\ product} \quad (6)$$

ii. Operating conditions of the reactor: The effect of the reactor's inlet pressure on selectivity was analyzed operating the reactor isothermally.

iii. Distillation column temperatures: A sensibility analysis of temperatures was carried out in order to favor the separation of undesirable products from acrolein. Thereby, for the distillation columns K-3 and K-4, the reboiler temperatures were studied taking into account the operating temperatures reported by the simulated shortcuts and the substances boiling points to achieve the separation at a lower cost. The condenser temperature of K-5 was also studied in order to break the acrolein-water azeotrope at a lower cost. The response parameters were acrolein losses after distillation columns and utility costs.

Acrolein losses for the distillation columns were calculated according to the following equation:

$$Acrolein\ losses = \frac{Feed\ column\ total\ molar\ flow - distillate\ column\ total\ molar\ flow}{Feed\ column\ total\ molar\ flow} \quad (7)$$

The data from the design and economic evaluation implemented in an Excel spreadsheet was synchronized with the data simulated in Aspen HYSYS to identify the operating conditions, temperature, at the lowest utility cost, low pressure steam or cooling water.

3. Results

3.1. Base case

The complete PDS is reported in Appendix A. Santa Marta, Colombia was chosen as the for the location due to the availability of raw materials, logistics, port infrastructure and the free trade zone of Santa Marta. Although acrolein production is not regulated directly, several agencies develop guidelines for hazardous chemicals using occupational exposure levels (OELs) [60].

The production plant was designed for an acrolein production of 4000 tons/year which are higher than the entire supply for the national market. Moreover, the international market might be composed by Venezuela and Honduras [45-46]. See details in Appendix A.

3.1.1. Conceptual design package

The conceptual design package includes the process diagrams (In-Out diagram and P.F.D.), the equipment design and the resulting equipment data-sheets and the financial analysis. The B.F.D. and the enlarged view of the P.F.D. for the glycerol purification and acrolein production processes can be found the Appendix B.

3.1.1.1. Input/output diagram

The input and output diagrams are shown in Figure 6 and 7. Those diagrams show the input and output flows from the process. It is possible to observe in Figure 6 that the crude glycerol components such as soap, methanol, etc. (see Table A2 and Figure A2) are removed and separated into separated streams and a purified glycerol flow is obtained. Furthermore, in Figure 7 it is seen that acrolein is not the only product in the process. Thus several separation steps are required in order to obtain a purified acrolein flow.

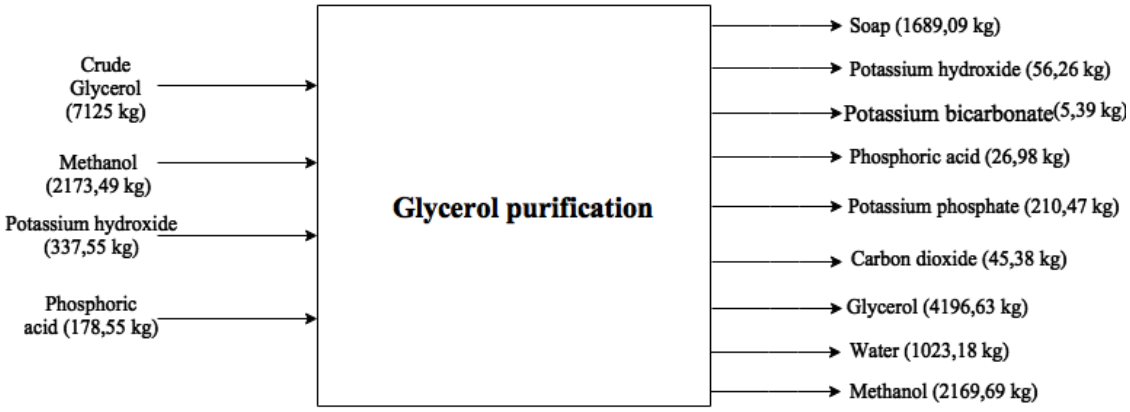


Figure 6. In-Out diagram of the glycerol purification process. Purified glycerol 4200 ton/year

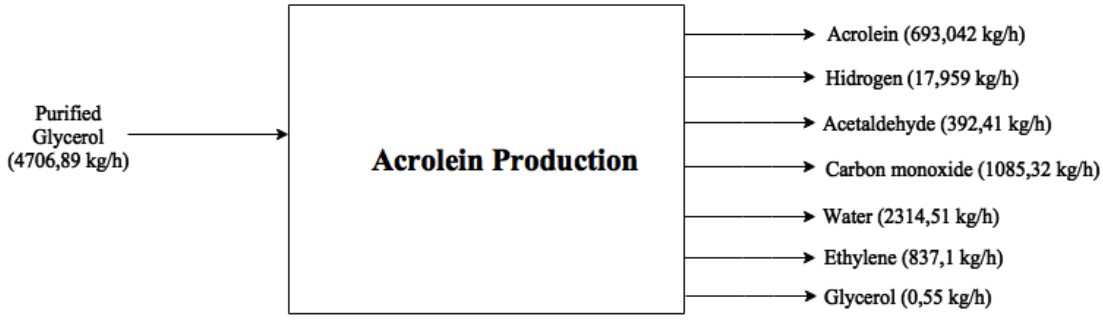


Figure 7. In-Out diagram of acrolein production process. Acrolein production 4000 ton/year

The economic potential was calculated taking into account the cost of raw materials and products (see Tables D1 and D2) and a contribution margin or economic potential of US $37 MM/year was found making the whole project attractive financially.

3.1.1.2. Equipment and plant costing

C-1 represents the saponification reactor where esters are removed from crude glycerol. F-1 represents a decanter where organics are separated from glycerol. This is followed by salt's neutralization reactor, C-2, where the salts are removed with a filter F-2, and the glycerol is fed to a distillation column K-1.

C-3 represents a packed bed reactor where glycerol is dehydrated in a presence of MFI as catalyst to produce acrolein and other products, this equipment uses low pressure steam as utility. V-1 represents the centrifugal compressor located after the reactor in order to increase the product's pressure. This compressor uses electricity as the utility. The product gas, continues to a fixed tube heat exchanger, W-4, which decreases the product´s temperature before the flash separator, K-2, and an absorption column, F-3, in order to separate non-condensable gases. The separator uses electric energy and the absorber uses water. The product liquids after the separation continues to the first distillation column K-3 in order to separate the gases from water. This column uses low pressure steam as utility. The gases continue to the second distillation column, K-4, in order to separate the light compounds. This column also uses low pressure steam and cooling water as utilities.

The product after the second distillation continues to an azeotropic extractive distillation column, K-5, which uses low pressure steam as utility in order to break up the acrolein-water azeotrope. The heavy compounds continue to a distillation column, K-6. This column also uses steam low pressure and cooling water as utilities. The liquid product from this column is conditioned and recycled into the azeotropic distillation column to favor the azeotropic separation. A simplified block diagram including all these units considered in the process is shown in Figure 8a.

The results of the equipment bare module costs (C_{BM}) were used to calculate the total module cost (C_{TM}), which does not consider the cost of site development. The C_{TM} was set as the fixed capital investment (FCI) of the project.

In Figure 8b, the bare module costs of the glycerol purification and acrolein production equipment were compared. The most expensive equipment is the compressor (V-1) due to the power necessary to increase the pressure of gases resulting of glycerol dehydration process. The neutralization reactor (C-2) is particularly expensive due to the fact that some gases are produced in this step needing a large area.

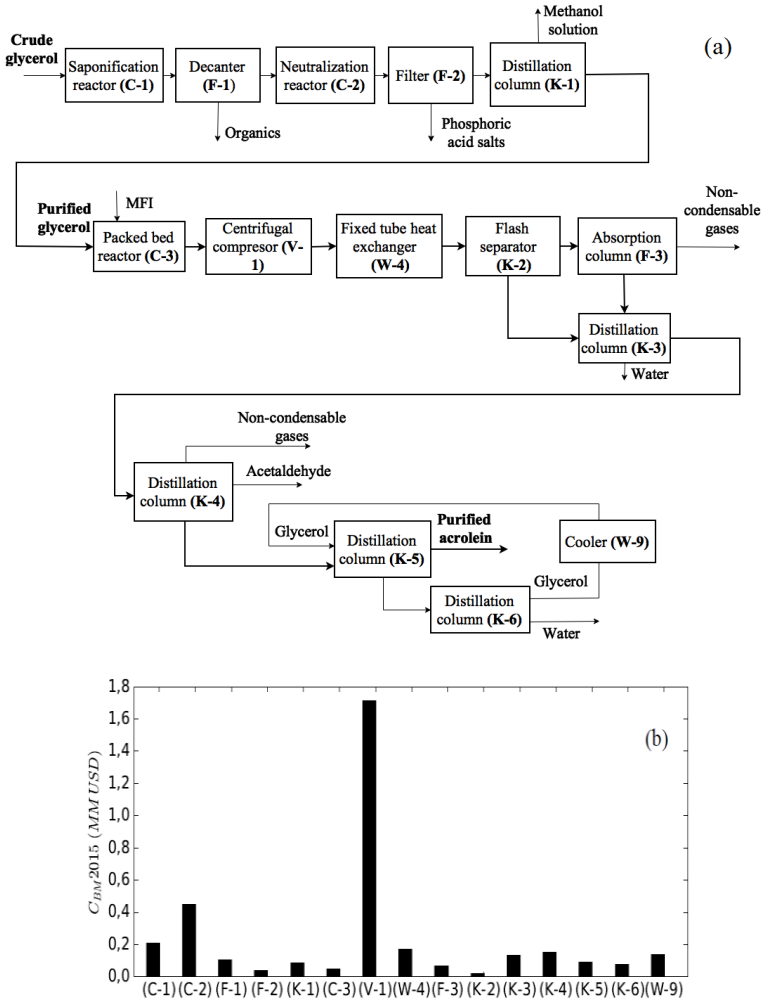


Figure 8. (a) Simplified block diagram of the complete acrolein production process. (b) Bare module cost (C_{BM}) of the process equipment.

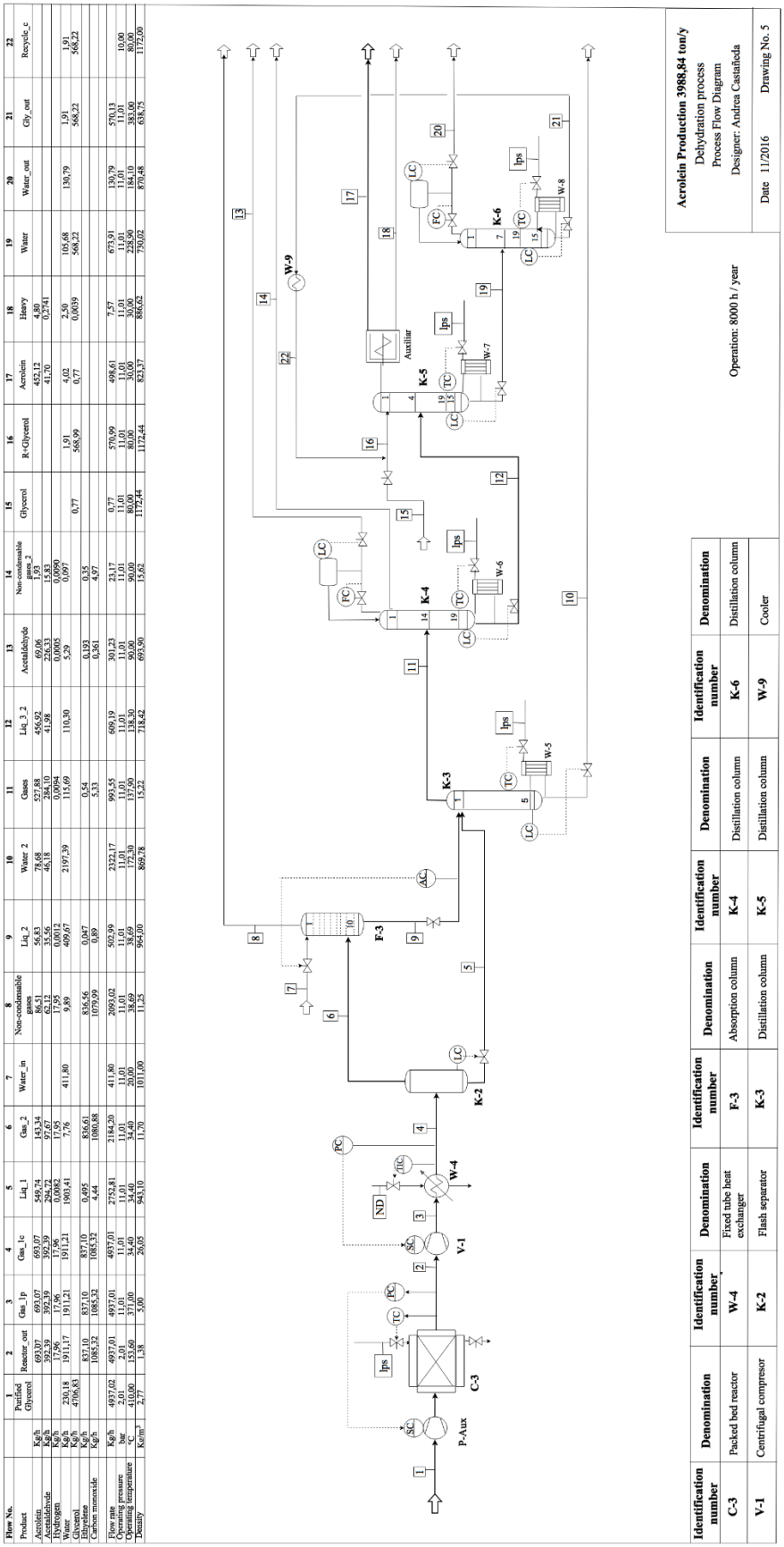
At the same time, labor costs ($C_{OL=}$ 0,55 MM USD/year), utility cost ($C_{UT=}$21 MM USD/year), cost of waste treatment ($C_{WT=}$1,93 MM USD/year), cost of raw material ($C_{RM=}$19,7 MM USD/year) were used to estimate the cost of manufacturing ($C_{OM=}$54,4 MMUSD/year). It is possible to see that the C_{UT} and the C_{RM} comprise most of the expenses due to the energy required to acrolein purification steps and the raw materials required to glycerol purification process. For further details about the general expenses see Appendix D.

3.1.1.3. Process flow diagrams and equipment specification

The diagrams shown in this section are built according to on the ISO 10628 standard [49].

Figures 9 and 10 show the P.F.D diagrams for the glycerol purification and acrolein production process. Enlarged views of the diagrams are shown in Figures B3 and B4.

Figure 9. Process flow diagram of the glycerol purification process



Flow No.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Product		Purified Glycerol	Reactor_out	Gas_1p	Gas_1c	Liq_1	Gas_2	Water_in	Non-condensable gases	Liq_2	Water 2	Gases	Liq_3_2	Acetaldehyde	Non-condensable gases_2	Glycerol	R-Glycerol	Acrolein	Heavy	Water	Water_out	Gly_out	Recycle_c
Acrolein	Kg/h		693,07	693,07	693,07	549,74	143,34		86,51	56,83	78,68	527,88	456,92	69,06	1,93			452,12	4,80				
Acetaldehyde	Kg/h		392,39	392,39	392,39	204,72	87,67		62,12	33,46	46,18	204,10	41,98	226,33	13,83			41,70	0,2741				
Nitrogen	Kg/h		3773,86	3773,86	3773,86	0,0007	0,0007		1737,95	0,0001		0,0000		0,0000	0,0000								
Water	Kg/h	230,18	1911,17	1911,21	1911,21	1903,41	7,76	411,80	9,89	409,67	2197,39	115,69	110,30	5,29	0,097		1,91	4,02	2,50	105,68	130,79	1,91	1,91
Glycerol	Kg/h	4706,83														0,77	568,99	0,77	0,0039	568,22		568,22	568,22
Ethylene	Kg/h																						
Carbon monoxide	Kg/h		837,10 1085,32	837,10 1085,32	0,495 4,44	836,61 1080,88			836,56 1079,99	0,047 0,89		0,54 5,33		0,193 0,861	0,35 4,97									
Flow rate	Kg/h	4937,02	4937,01	4937,01	4937,01	2752,81	2184,20	411,80	2093,02	507,99	2322,17	993,55	669,19	301,23	23,17	0,77	570,99	498,61	7,57	673,91	130,79	570,13	10,00
Operating pressure	bar	2,01	2,01	1,01	1,01	1,01	1,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01
Operating temperature	°C	147,00	155,60	37,00	30,00	34,40	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00	30,00
Density	Kg/m³	2,77	1,38	5,00	26,05	943,10	11,70	1011,00	11,25	964,00	869,78	15,22	718,42	693,90	15,62	1172,44	1172,44	823,37	886,02	750,02	870,48	638,75	1172,00

Identification number	Denomination
C-3	Packed bed reactor
V-1	Centrifugal compresor

Identification number	Denomination
W-4	Fixed tube heat exchanger
K-2	Flash separator

Identification number	Denomination
F-3	Absorption column
K-3	Distillation column

Identification number	Denomination
K-4	Distillation column
K-5	Distillation column

Identification number	Denomination
K-6	Distillation column
W-9	Cooler

Figure 10. Process flow diagram of the base case acrolein production process

Equipment specification data sheets show the most relevant information of the process equipment, such as operating conditions and the construction material. The specification data sheets for Figure 9 is shown in Tables C1-C5 and for Figure 10 in Tables C6-C15.

Taking into account that the acrolein is a very corrosive compound all the process units were designed with austenitic stainless steel (SS) which is not easily corroded by acrolein and it can be resist temperatures until 450°C. Stainless steel is heat and corrosion-resistant, noncontaminating, and easily fabricated into complex shapes [61].

3.1.2. Simulation

Figures 3 and 4 show the simulation flowsheet of the glycerol purification process and acrolein production process performed in Aspen HYSYS. The names of the streams and equipment shown in the figures correspond to the ones shown in the P.F.Ds. Nevertheless, the simulation includes auxiliary equipment not included in the process diagrams.

The first process begins feeding the raw materials for the glycerol purification (see Figure 3). Raw glycerol was fed into reactor at 25°C and solid potassium hydroxide is dissolved in methanol and added under stirring to the reactor to start saponification of the esters. The reaction mixture continues to a decanter where potassium hydroxide and soaps are separated from glycerol at standard conditions (25°C, 1 bar). The mixture is neutralized with concentrated phosphoric acid. Precipitated salts are removed by filtration and the excess methanol is distilled in K-1.

Figure 11 shows in detail K-1 as used in the simulation. The condenser was defined as total and it was fixed a distillate rate of 123,5 kgmol/h and a reflux ratio of 0,2 in order to obtain a distillate with 68 wt.% of methanol. Then, the bottom product was cooled to 30°C and diluted with water to feed the second process (acrolein production). The resulting purified glycerol was fed into a reactor, 87% of glycerol conversion for reaction 1 (Equation 1) was obtained.

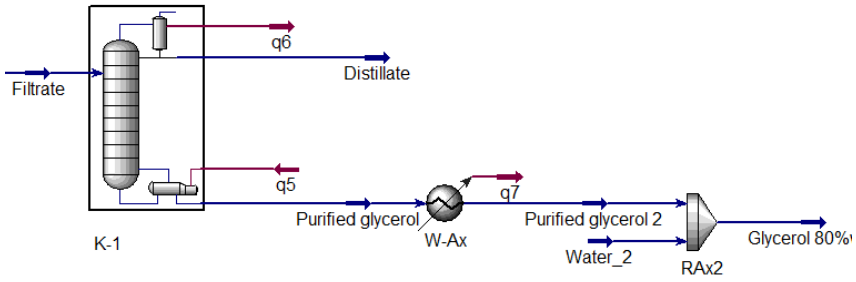


Figure 11. Close-up view of the simulated distillation column K-1.

In order to separate non-condensable gases, a water flow was fed at the top of the absorber column as shows in detail in Figure 12. Therefore, 50 wt.% of carbon monoxide and 40% of ethylene were removed from the feed stream.

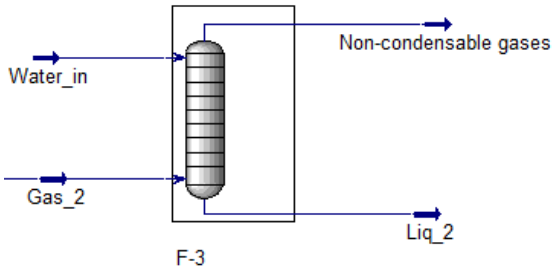


Figure 12. Close-up view of the simulated absorber column F-3

The liquids obtained were fed to K-3 where the water was removed and distillate was fed to K-4, which had a partial condenser in order to remove acetaldehyde as a light compound with a purity of 72 wt.%. The bottom stream was cooled using an auxiliary cooler before continuing until K-5, where the acrolein-water azeotrope was broken using glycerol as entrainer. The liquid-liquid equilibrium formed requires the use of a sub flowsheet due to the different binary interaction parameters for the extended NRTL model required to describe this behavior. In order to accurately predict the phase separation, this sub flowsheet used the parameters determined using UNIFAC LLE calculations. A close-up view of the azeotropic distillation and sub flowsheet are shown Figure 13. In the output stream acrolein at 90 wt.% was obtained.

The bottoms product from K-5 continue to K-6 where glycerol and water were separated and glycerol was recycled back to K-5, recovering 97% of the mass flow of glycerol. At the same time, a glycerol stream was fed in a mixer (R-2) in order to make up the glycerol losses.

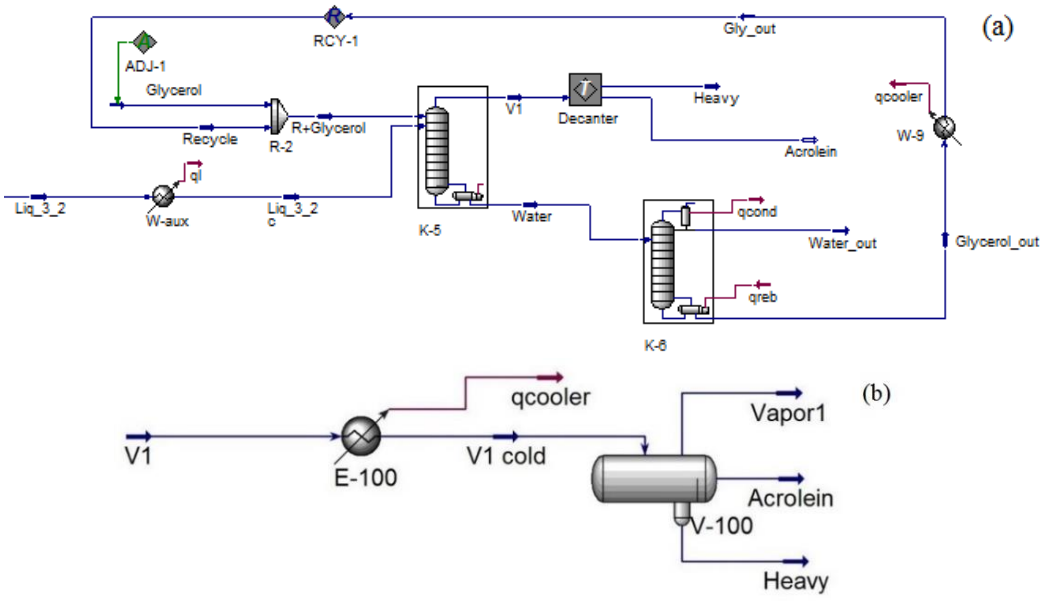


Figure 13. (a) Close-up view of the simulated azeotropic distillation (b) Close-up view of the simulated sub flowsheet

3.1.3. Economic evaluation

The initial investment was calculated by adding the costs of land, the FCI (CTM) and the working capital (WC). The required initial investment for the base case was $4 MM USD. The cash flow statement was calculated for a 12-year period, with a startup at the second year. At the same time, a depreciation of 10 years was fixed yearly according to Turton et al. [48]. For further details about the considerations to estimate the cash flow, see Tables E1 and E2. Figure 14 shows the cash flow statement during a 12-year period. The effective annual interest rate, considered for this case was 10%.

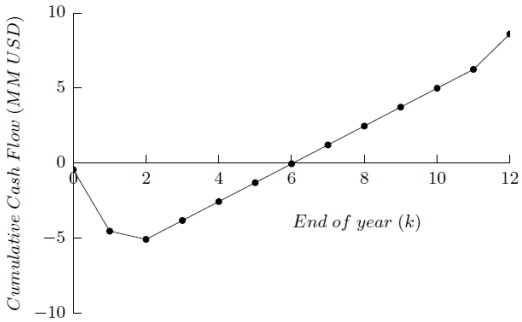


Figure 14. Cash flow statement for the base case design during a 12-year period

The revenues obtained in the project come from the acrolein, acetaldehyde and phosphoric acid salts. The latter is obtained from the neutralization step during glycerol purification. It is important to note that the sale price of acetaldehyde and crystals were fixed to 1.000 US/ton and 50 USD/ton respectively according to information available in the market [62]. However, the sale price of acrolein can fluctuate between $13300 USD/ton-$13650 USD/ton according to the market references [63]. Figure 15, shows the differences of the IRR with changes in the price of acrolein. The raw material prices were fixed, according to the information available in the market (see Table D2).

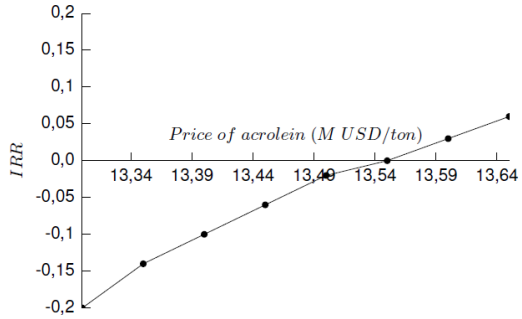


Figure 15. Price of acrolein vs. IRR

The profitability for the base case design of this project was determined using IRR and NPV. The NPV was $155 MM USD and the IRR was 6%. Therefore, the project is not feasible for the base case.

3.2. Optimized case

3.2.1. Reactor length

Figure 16 shows acrolein selectivity and acrolein mole fraction at different reactor lengths at constant pressure for an adiabatic reactor with an inlet temperature of 410°C. Up to 4m of reactor length, acrolein selectivity and mole fraction decrease, whereas from 4m to 9m remain constant until 9m. After 9m acrolein selectivity tends to 0%, because of side reactions of acrolein to produce carbon monoxide and ethylene (Equation 2). Therefore, the reactor length should be fixed below 4m. There are two circles drawn in Figure 16, the dashed one indicates the selectivity obtained in the base case where the length was 10 m and the other one indicates the selectivity obtained in the optimized case, 1m length. Therefore, acrolein selectivity increased from 0,064 to 0,19.

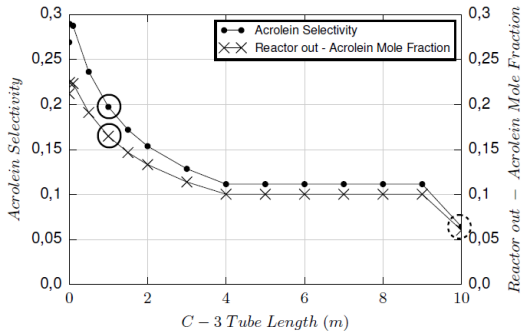


Figure 16. Calculated acrolein selectivity and mole fraction at different reactor lengths at T_{in}=410°C, T_{out}=153,6°C and 2,013 bar. Simulated points for the base case (dashed circle) and optimized conditions (continuous circle).

3.2.2. Operating conditions of the reactor

The reactor operation in the base case was carried out at adiabatic conditions with an inlet temperature of 410°C, and it was decided to simulated the reactor at isothermal conditions at 410°C to understand the effect of temperature on the selectivity of the process. Similarly, to the adiabatic case, the reactor volume was varied in order to determine its effect on selectivity.

Figure 17 shows that up to 0,1 m and 410°C, acrolein selectivity decreases rapidly and above 0,1 m acrolein selectivity tends to 0%. Therefore, the isothermal conditions for the reactor were not included in the optimization due to the unfeasible dimensions for obtained a good selectivity.

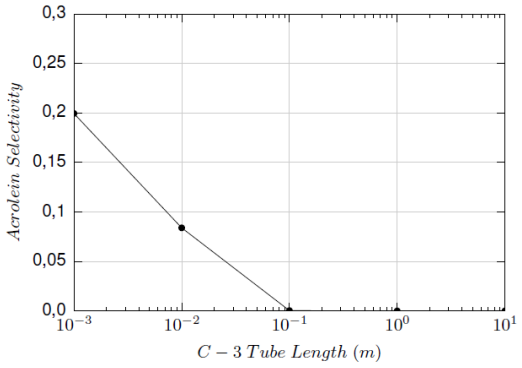


Figure 17. Acrolein selectivity at 2,013 bar, 410°C and different reactor lengths.

3.2.3. Sensitivity analysis

Acrolein losses and utility costs were calculated at different reboiler temperatures in K-3 and K-5, and different condenser temperatures in K-4 in order to improve the acrolein recovery after purification.

3.2.3.1. Temperature distillation column K-3

In K-3, the water added in F-3 is removed in the bottoms in order to (i) obtain an outlet gas stream of acrolein with low contents of water and (ii) decreased losses of acrolein after distillation. Therefore, the reboiler temperature was modified and the acrolein losses and utility costs in K-4 were monitored.

Figure 18 shows that at 140°C acrolein losses are 100% whereas the cost of utility (low pressure steam for the reboiler) is one of the lowest. Above 150°C acrolein losses and cost of utilities decrease. However, it is important to take into account that the boiling point of water at the operating pressure (11,01 bar) is 183.9 °C. In order to avoid leaking through the gases stream, a temperature of 173 °C was chosen. The base case reboiler temperature was 172,3°C and the optimized case where the bottom or reboiler temperature was 173,1°C, thus acrolein losses decreased from 0,6% to 0,5% at a lower utility cost.

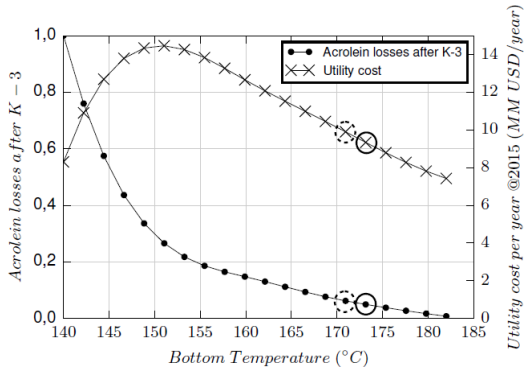


Figure 18. Acrolein losses and cost of utilities for K-3 at different reboiler temperatures and 11,01 bar. Simulated points for the base case (dashed circle) and optimized conditions (continuous circle).

3.2.3.2. Temperature distillation column K-4

Undesirable products (acetaldehyde and non-condensable gases) are removed at K-4 in the distillate. Therefore, the effect of the condenser temperature was evaluated considering the cost of utilities and acrolein losses in K-4.

Figure 19 shows that acrolein losses and cooling water increase with temperature increases. However, the cost of steam remains almost constant. Therefore, the operating temperature should be kept below 65°C. For the base case the temperature was 90°C and for the optimized case was 62,5°C. Acrolein losses decreased from 0,11% to 0,08% at a lower utility cost.

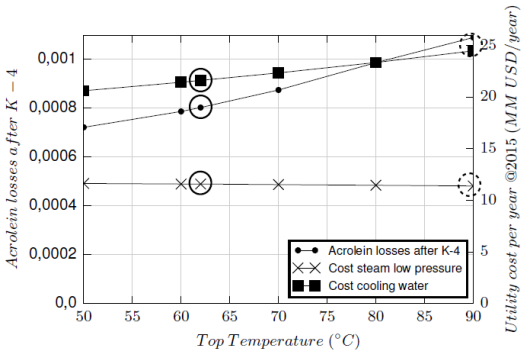


Figure 19. Acrolein losses and cost of utilities for K-4 at different condenser temperatures and 11,01 bar. Simulated points for the base case (dashed circle) and optimized conditions (continuous circle).

3.2.3.3. Temperature distillation column K-5

The acrolein losses and utility cost per year at different reboiler temperatures were analyzed. Figure 20 shows that acrolein losses after K-5 and the cost of the utility (low pressure steam) increases with temperature in the reboiler. At 11,01 bar acrolein's boiling point is 151,3°C and water's boiling point is 183,9°C. Thereby, the operation temperature should be kept above 151 °C to favor the separation process. The base case temperature was 195°C and for the optimized case was 188°C. Acrolein losses decrease from 27% to 20%.

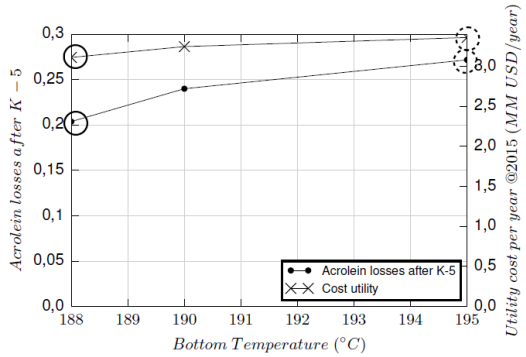


Figure 20. Acrolein losses and cost of utilities for K-5 at different reboiler temperatures and 11,01 bar. Simulated points for the base case (dashed circle) and optimized conditions (continuous circle).

3.2.4. Optimal parameters

The optimal reactor length was 1m, this allowed to obtain an acrolein selectivity (0,19) three times higher than in the base case (0,064) operating at isobaric conditions. For the purification section, which mainly involves the distillation columns K-3, K-4 and K-5, the optimal temperatures were 173°C (reboiler temperature), 62°C (condenser temperature) and 188°C (reboiler temperature), respectively. The lower costs were achieved considering thermodynamic limitations, thereby it was possible to recover 74% of the acrolein produced compared to 65% in the base case. Moreover, the purity of the produced acrolein increased from 90 to 92 wt.%. For the by-product, acetaldehyde, the recovery increased from 60 to 75% and the purity also increased from 72 to 99 wt.%.

3.2.5. Optimized case design and plant costing

The cost of the equipment and the plant for the acrolein production process, which include the glycerol purification were calculated for the optimized process in order to compare both processes. Figure 21 shows the bare module cost of the process equipment for the base case design compared to the optimized case. V-1 (centrifugal compressor) and C-2 (neutralization reactor) are still the most expensive equipment in the process. In the optimized case design, it is possible to note that the costs of distillation columns K-3, K-4 and the heat exchanger W-9 increase due to the higher column temperatures in the optimized case.

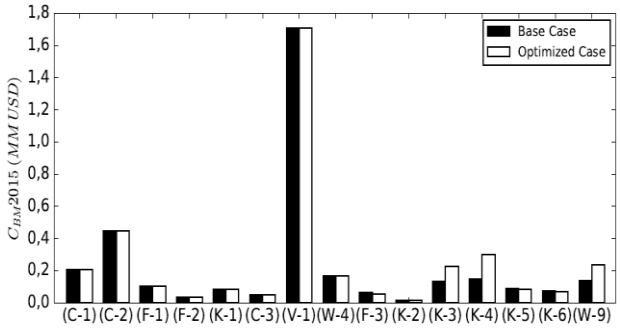


Figure 21. Bare module cost (C_{BM}) of the process equipment for base case design (black bars) and optimized case design (white bars). Equipment names correspond to those in Figure 8a.

For the optimized case labor costs ($C_{OL=}$ 0,55 MM USD/year) and cost of raw material ($C_{RM=}$19,7 MM USD/year) did not change compared to the base case. However, utility costs increased 40% ($C_{UT=}$29,4 MM USD/year) and the cost of waste treatment decreased 30% ($C_{WT=}$1,4 MMUSD/year). The cost of manufacturing for the entire process increased almost 20% ($C_{OM=}$64 MM USD/year).

Figure 22 shows the comparison of general expenses for the base case and optimized case where the cost of utilities increases due to changes in the distillation columns and the cost of waste treatment decreased due to the acrolein and acetaldehyde recovery. The cost of labor and raw materials remained constant because no changes in the topology of the system were made.

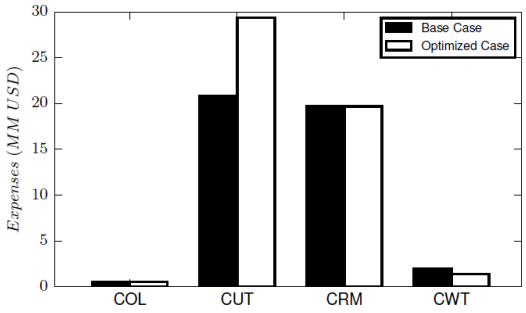


Figure 22. Comparison of the cost of labor (C_{OL}), utilities(C_{UT}), waste treatment (C_{WT}) and raw materials (C_{RM}) for the optimized (white bars) and base case (white bars).

3.2.6. Economic evaluation

The required initial investment for the optimized case design was $4.5 MM USD, 13% higher than for the base case. A comparison of the cash flows for the base case and optimized case is shown in Figure 23.

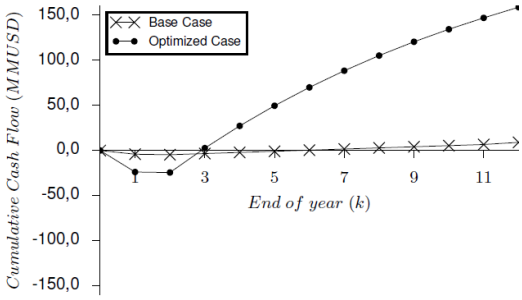


Figure 23. Cash flow statement during a 12-year period

The cash flow of the optimized case has a larger increase than the base case cash flow for the same period of time. The process' IRR increased from 6% for the base case to 58% for the optimized case due to the increase production of acrolein and acetaldehyde. Figure 24 shows two diagrams with Sankey representation where the thickness of the line means the amount of the substance in the stream and it is possible to see that the amount of acrolein increased notably in comparison with the base case. Despite a larger consumption of utilities, the higher revenue generated by the increased recovery of the products increases the profitability of the project.

The optimized case had a NPV of $420 MM USD, almost 3 times larger than that of the base case.

The acrolein price could be reduced in order to compete with the international market, to a value greater than $5.900 USD/ton to keep a NPV above zero and a IRR of 10%.

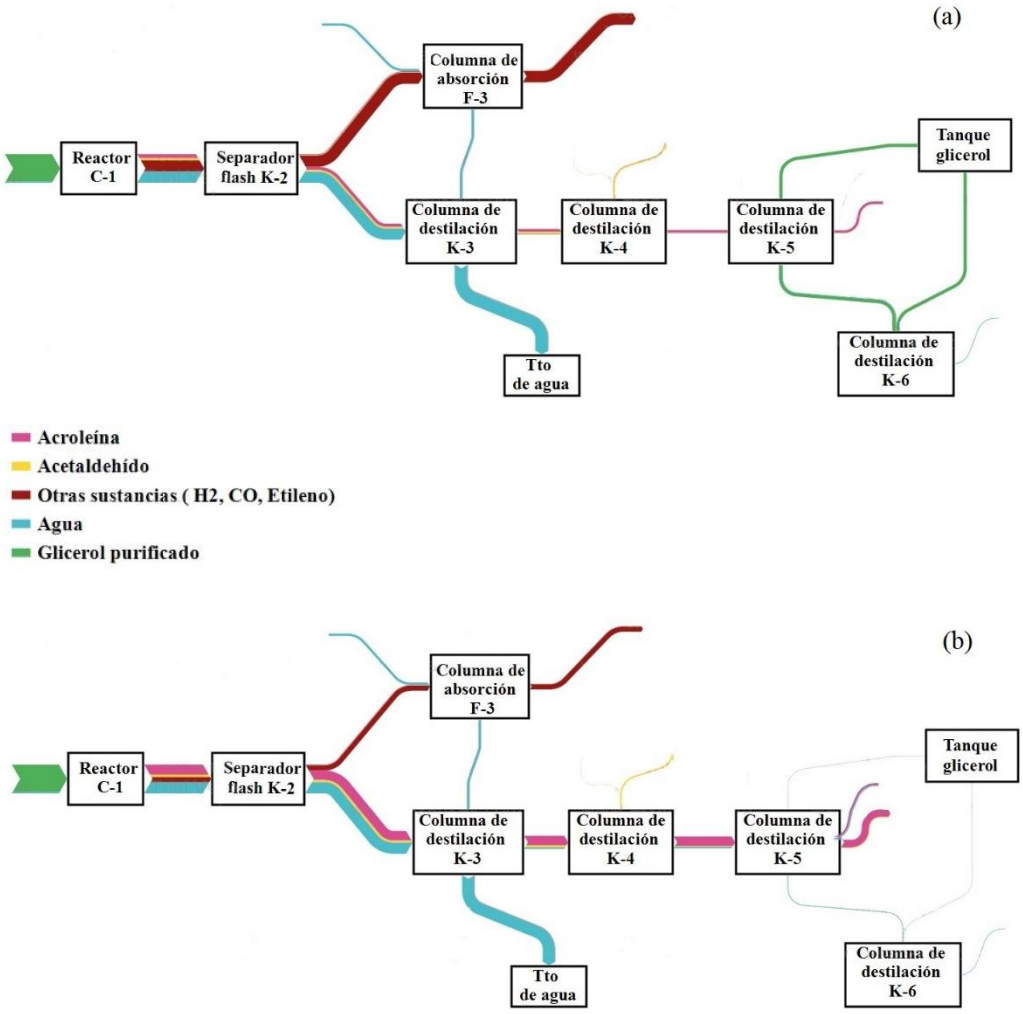


Figure 24. Sankey representations for acrolein production process (a) Base case, (b) Optimized case

4. Conclusions

Acrolein is an important precursor of chemicals such as methionine. It is commonly produced from petroleum derived propylene. Using bioglycerol from the biodiesel process presents an opportunity to replace a petroleum based raw material improving thereby the profitability and sustainability of the whole process of acrolein production. In order to assess the feasibility of the process, a plant for the production of acrolein from bioglycerol has been designed, simulated and optimized.

A small packed bed reactor (1m length and 0,3m diameter) was required in order to obtain high selectivity towards acrolein using a MFI zeolite as a catalyst. The outlet stream from the reactor has to be purified using a flash separator, an absorption column and four distillation columns in order to obtain pure acrolein and acetaldehyde.

The reactor length, reboiler temperatures of K-3 and K-5 and condenser temperature of K-4 were chosen as variables susceptible to be optimized, because these determine a high selectivity and the desirable purification of acrolein. Optimization increased acrolein selectivity from 0,06 to 0,19. Also, the recovery of the produced acrolein was increased from 65% to 74%. The NPV was increased almost threefold and the IRR increased from 6% to 58%.

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Appendix A. Project design specifications (PDS)

A.1. Physicochemical properties

The physicochemical properties of raw materials and main products involved in the crude glycerol purification and glycerol dehydration are shown in Table A1, which describes the physical state, molecular weight, color, boiling point, melting point, critical temperature, vapor pressure and density at standard conditions.

Table A1. Physicochemical properties of raw material and principal products

[38, 64-68]

	Crude glycerol purification			**Glycerol dehydration**		
Physicochemical properties	**Methanol**	**Potassium hydroxide**	**Phosphoric acid**	**Glycerol**	**Acrolein**	**Acetaldehyde**
Physical state	Liquid	Solid (Solid pellets)	Liquid (Syrupy liquid Viscous liquid.)	Liquid (Viscous (Syrupy) liquid.)	Liquid	Liquid (Fuming liquid.)
Molecular weight (g/mol-g)	32,04	56,11	Not applicable			
Color	Colorless	White	Clear Colorless	Clear Colorless	Colorless to light yellow	Colorless
Boiling point (°C)	64,5	1384 (Descomposition temperature)	158	290	52.5	21
Melting point (°C)	-97,8	380	21	19	-88	(-123,5)
Critical temperature (°C)	240	Not available	Not available	Not available	254	188
Vapor pressure (bar)	12,3 kPa (@ 20°C)	Not available	0,3 kPa (@ 20°C)	0 kPa (@ 20°C)	28 kPa (@ 20°C)	101,3 kPa (@ 20°C)
Density (kg/m^3)	792	2120	1880	1261	0.8427	788

It is important to note that the glycerol resulting from biodiesel production is not pure, thus the composition of crude, purified and commercial glycerol are shown in Table A2. The parameters of crude glycerol were used to determine the purification before the acrolein production process.

Table A2. Glycerol composition [69]

Parameter	Crude glycerol	Purified glycerol	Refined/commercial glycerol
Glycerol content (%)	60–80	99,1–99,8	99,20–99,98
Moisture content (%)	1,5–6,5	0,11–0,8	0,14–0,29
Ash (%)	1,5–2,5	0,054	<0,002
Soap (%)	3,0–5,0	0,1–0,16	0,04–0,07
Acidity (pH)	0,7–1,3	0,10–0,16	0,04–0,07
Chloride (ppm)	ND	1.0	0,6–9,5
Color (APHA)	Dark		

Secondly, in the glycerol dehydration process to obtain acrolein, MFI zeolite is used as the catalyst, thus, the physicochemical characteristics are shown in Table A3.

Table A3. Physicochemical characteristics of catalysts [27]

Properties	MFI
Density (kg/m^3)	720
Void fraction	0,75
Si/Al	50
BET surface area (m^2/g)	70
Micropore volume (cm^3/g)	0,027
Zeolite content	15
Rare earth content, wt%	-
Particle size (μm)	40-120

The zeolite is deactivated due to the coke deposition in reaction 3 (Equation 3), Corma et al. [27] proposed that the glycerol dehydration process to be carried out in a circulating bed reactor with continuous catalysis regeneration, a system similar with the one used in the fluid catalytic cracking of hydrocarbons. It is important to note that Equation 3 was not considered in the simulations, therefore if the reaction were included, it would be necessary a restructuration of the process in the reaction section in order to implemented the catalysis regeneration system.

A.2. Transport and safety regulations

International regulations for transport of dangerous good are shown below, it is important to note that Colombia has national regulation for transport of dangerous goods which regulates the packing, labelling and incompatible substances such as: Decree 1079/2015 [83] and Colombian Technical Norm (NTC in its Spanish acronym) 1692/2015 [84].

- **Glycerol**

Transport regulations

According to the Occupational Safety and Health Administration (OSHA), Glycerol is a product that does not contain a hazardous material. The material does not appear to be subject to the HMR (Hazardous Materials Regulations) as defined by the U.S Department of transportation [72].

United Nations recommendations for the transport of dangerous goods

Not classified according to the United Nations Recommendations on the Transport of Dangerous Goods [73].

- **Acrolein**

Transport regulations

Acrolein is unlikely to be transported over long distances because of its high reactivity and estimated short half-live on air and water, and due to it, acrolein does not tend to persist in the environment, and its intercompartmental movement is small:

Air: Acrolein emitted to air reacts primarily with hydroxyl radicals generated in the troposphere photo chemically. Minor processes include direct photolysis, reaction with nitrate radicals, and reaction with ozone. Acrolein has been detected in rainwater, indicating that it may be removed by wet deposition. The calculated atmospheric half-life of acrolein, based on rate constants for hydroxyl radical reaction, is between 3,4 and 33,7 h. The overall reactivity-based half-life of acrolein in air, is less than 10 h. Based on these short estimated half-lives, acrolein is not a candidate for long.-range atmospheric transport [74].

Water: Acrolein is removed from surface water primarily by reversible hydration, biodegradation by acclimatized microorganisms, and volatilization. In groundwater, acrolein is removed by anaerobic biodegradation and hydrolysis. The overall reactivity-based half-life of acrolein in surface water is estimated to be between 30 and 100 h. In groundwater, half-lives of 11 days and 336–1344 h (14–56 days) are estimated based on aerobic and anaerobic degradation, respectively. Observed dissipation half-lives of acrolein applied as an herbicide in irrigation canals range from 7,3 to 10,2 h. The relatively short observed half-lives of acrolein in surface waters make long-range aquatic transport unlikely [74].

United Nations recommendations for the transport of dangerous goods

The United Nations Committee of Experts on the Transportation of Dangerous Goods and the International Maritime Organization classify acrolein as a flammable liquid (Class 3 and 3,1 respectively) with subsidiary risk as a poisonous substance. Acrolein is also classified as a very dangerous substance for packing purposes (Packing Group I). Packing methods and labels are recommended [75]. The recommended labels are:

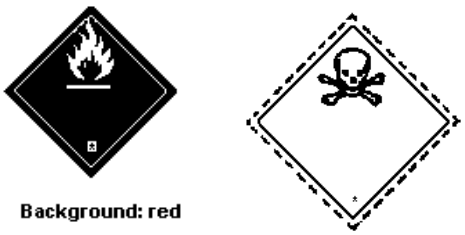


Figure A1. Labels recommended for United Nations [75]

Also, the United Nations counts with a specified system of classification for each dangerous good organized on a table, as shown below [76].

Table A4. United Nations recommendations on the transport of dangerous goods for acrolein [76]

UN No.	Name and description	Class or division	Subsidiary risk	UN packing group	Special provisions	Limited and excepted quantities		Packaging's and IBC's		Portable tanks and bulk containers	
								Packaging instruction	Special packaging provisions	Instructions	Special provisions
(1)	(2)	(3)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9)	(10)	(11)
1092	ACROLEIN, STABILIZED	6,1	3	I	354	0	E0	P601		T22	TP2 TP7 TP13 TP35

Note: For further details, see [77].

- **Acetaldehyde**

Transport regulations

Intercompartmental transport of acetaldehyde is expected to be limited because of its high reactivity. However, some transfer of acetaldehyde to air from water and soil is expected, because of its high vapor pressure and low sorption coefficient [78].

United Nations recommendations for the transport of dangerous goods

The United Nations counts with a specified system of classification for each dangerous good organized on a table, as shown below.

Table A5. United Nations recommendations on the transport of dangerous goods for acetaldehyde [76]

UN No.	Name and description	Class or division	Subsidiary risk	UN packing group	Special provisions	Limited and excepted quantities		Packaging's and IBC's		Portable tanks and bulk containers	
								Packaging instruction	Special packaging provisions	Instructions	Special provisions
(1)	(2)	(3)	(4)	(5)	(6)	(7a)	(7b)	(8)	(9)	(10)	(11)
1089	ACETALDEHYDE	3		I		0	E3	P001		T11	TP2 TP7

Note: For further details, see [77].

A.3. Plant location

Santa Marta, Colombia has been chosen as the plant's site location due to the availability of raw materials, the logistics and port infrastructure and the free trade zone of Santa Marta. However, if the transport costs were including in the economic analysis, it will be necessary a comparison between potential places to define the best plant location. Colombia is considered by the World Bank as the country with the best business environment in Latin America, according to the Doing Business Report 2015 [79]. Table A6 shows the main information and characteristics of the chosen location and Figure A2 shows the geographical location.

Table A6. General information about Santa Marta

City	Santa Marta
Department	Magdalena
Temperature	Temperature range: 28 ° C and 33 ° C [80]
Atmospheric pressure	760 mmHg [80]
Altitude	2 msnm (min)-5,775 msnm (max) [80]
Wind speed media	3,0 m/s (Annual average) [80]
Solar radiation	5-5,5 kWh/m2 [81]

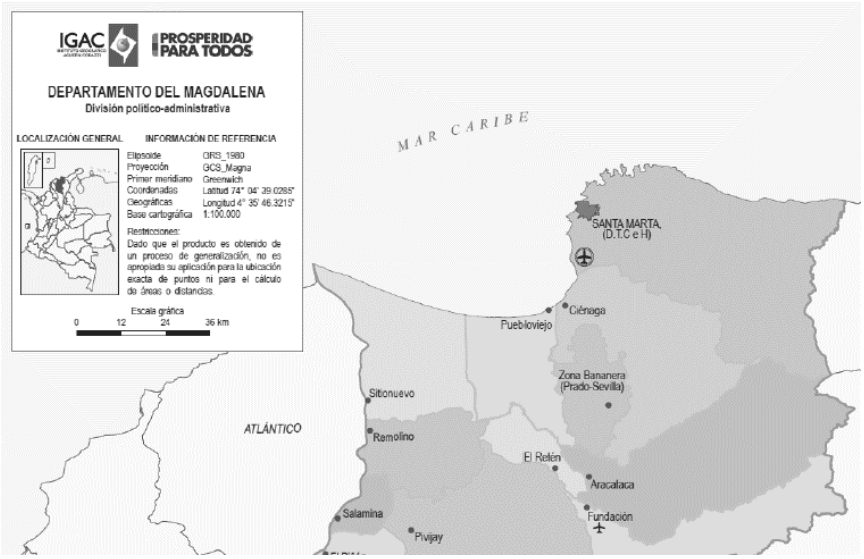


Figure A2. Geographical location of Santa Marta [82]

In Santa Marta or near it, there are wide availability of suppliers of crude glycerol as raw material derivate from biodiesel production. The biodiesel producers in Colombia are shown in Table A7.

Table A7. Main places in Colombia where Biodiesel from Palm is produced [83]

Region	Company	Capacity (Ton/year)
North, Codazzi	Oleoflores	60.000
North, Santa Marta	Biocombustibles sostenibles del Caribe	100.000
North, Santa Marta	Odin Energy	36.000
Central, Barrancabermeja	Ecodiesel de Colombia	120.000
Eastern, Fotacativa	BioD	120.000
Eastern, San Carlos de Guaroa (Meta)	Aceites Manuelita	120.000
Eastern, Castilla la nueva (Meta)	Biocastilla	15.000

Furthermore, the more convenient way to export in Colombia is through the seaports. Figure A3 shows the main seaports of the Colombian Caribbean.

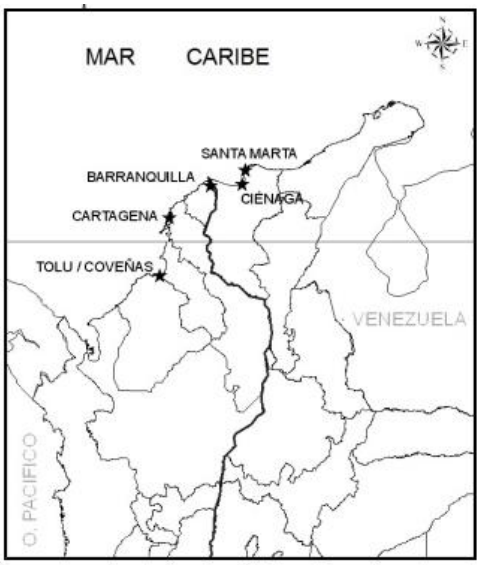


Figure A3. Ports in the Caribbean sea, Colombia [84]

Colombia has a competitive number of free trade zone within which lies the free trade zone of Santa Marta. This is a permanent free trade zone and it is declared as such until June 29, 2024 [85]. Free trade zone provides the following benefits to projects producing goods or services to be installed on them [86]: Income tax rate of 15%; no cause or pay customs duties (Value-added tax (VAT) and custom tariff) for goods brought into the free zone from outside; IVA exemption for raw materials, inputs and finished goods acquired in the national customs territory; the exports made from free trade zone to third countries are likely to benefit from international trade agreements signed by Colombia. Colombia free trade zones are governed by special regulations, consisting of laws, decrees and resolutions which are available on the website of the ministry of commerce, industry and tourism [86].

A.4. Applicable taxes in Colombia

Taking into account the district tax statute of Santa Marta, in the article 63. Taxes for industrial activity, according to the code 1110 of taxes for industrial activities, it indicates a monthly tax of 7x1000 (COP) [87, Sec. Artículo 63].

A.5. Applicable laws and resolutions

The acrolein production is not regulated directly by Colombia, due to it is not an acrolein manufacturer. Besides, acrolein is considered toxic to humans following inhalation, oral or dermal exposures. Acute (short-term) inhalation exposure may result in upper respiratory tract irritation and congestion, thus, several agencies develop guidelines or objectives for hazardous chemicals using occupational exposure levels (OELs) [60]. Nevertheless, in Colombia exists laws and resolutions for transport of dangerous goods which regulates the packing, labelling and incompatible substances [83-84]. Other conditions about utilities, construction and safety and health at work are reported below:

Table A8. Applicable laws and resolutions in Colombia

Laws and resolutions	Content
Occupational health and safety management system	
Law 1562:2012	Labor risk prevention
Resolution 2646:2008	Risk evaluation
Decree 2566:2009	Occupational diseases
OHSAS 18001:2007	Occupational health and safety management systems – implementation training
Utilities	
Resolution N°9 0807:2013	Technical Regulations of Electrical Installations (RETIE in Spanish)
Resolution 898:2015	Environmental criteria for fuels using in boilers (Low pressure steam)
Environmental regulations	
Decree 2:1982	Atmospheric emissions
Decree 948:1995	Air-pollution control and prevention
Decree 3930:2010	Water uses and liquid waste
Decree 1541:2008	Water uses
Construction	
NSR-10	Colombian regulations for earthquake-resistant construction

A.6. Market analysis

In order to estimate the national demand for acrolein and acetaldehyde in 2016 and identify the international markets, a market analysis was carry out. It was taken the reported exports and imports for acetaldehyde and acrolein which are represented by graphics below.

- **Acrolein**

According to the information reported in BACEX database [75], the companies that exported acyclic aldehyde in Colombia in 2015 and 2016 are Tauroquímica S.A.S., Lipesa Colombia and Suministros mineros latinoamericanos S.A.S. Figure A4 depicts the main destinations for the acyclic aldehyde exported from Colombia in the years 2015 and 2016. Venezuela, Dominican Republic, Peru and Ecuador are Colombia's main destinations for acyclic aldehyde exports.

At the same time the main companies that imported acyclic aldehyde to Colombia in 2015 and 2016 are Symrise ltda and Firmenich S.A. Figure A5 it is possible to see that Germany seem to be the main acyclic aldehyde supplier.

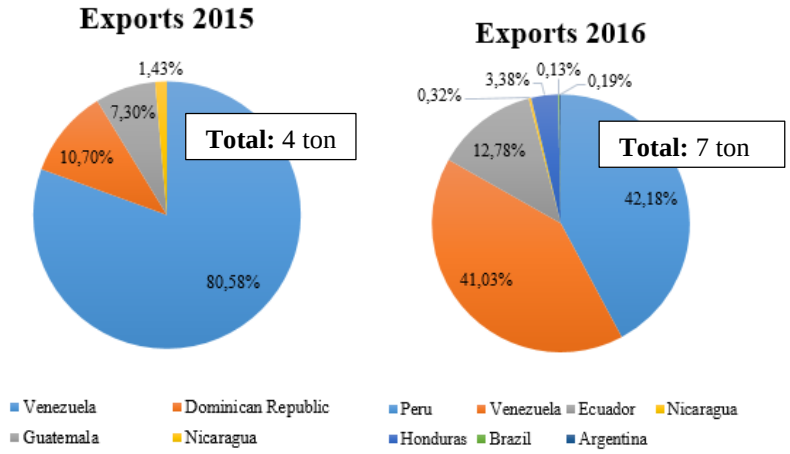


Figure A4. Reported exports of acyclic aldehyde

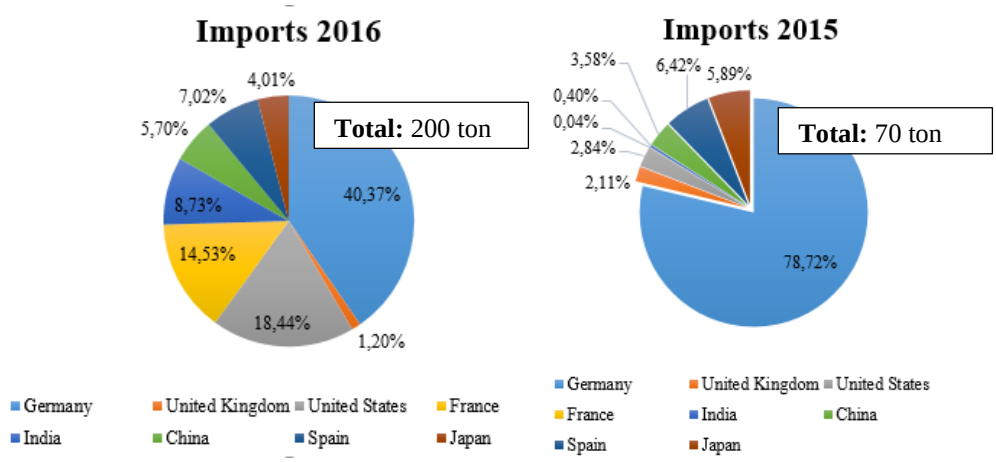


Figure A5. Reported imports of acyclic aldehyde

- **Acetaldehyde**

According to the information reported in BACEX database [46], the company that exported acetaldehyde in Colombia in 2015 is Callizo aromas S.A.S. Figure A6 depicts the main

destinations for the acetaldehyde exported from Colombia in the year 2015. Venezuela is Colombia´s main destination for acetaldehyde exports.

At the same time the main companies that imported acetaldehyde to Colombia in 2015 and 2016 are Lucta Grancolombia S.A.S, Productora nacional de aromas fragancias y colorantes S.A. and Elementos químicos LTDA. Figure A7 it is possible to see that United Kingdom and Spain seem to be the main acetaldehyde suppliers. In 2015 most imports proceeded from United Kingdom, while in 2016 most imports proceeded from Spain.

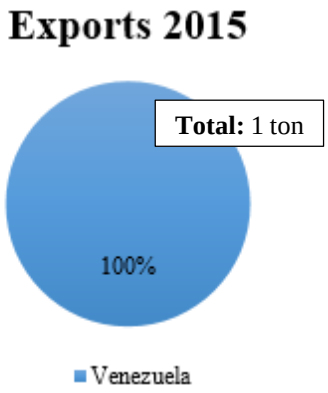


Figure A6. Reported exports of acetaldehyde

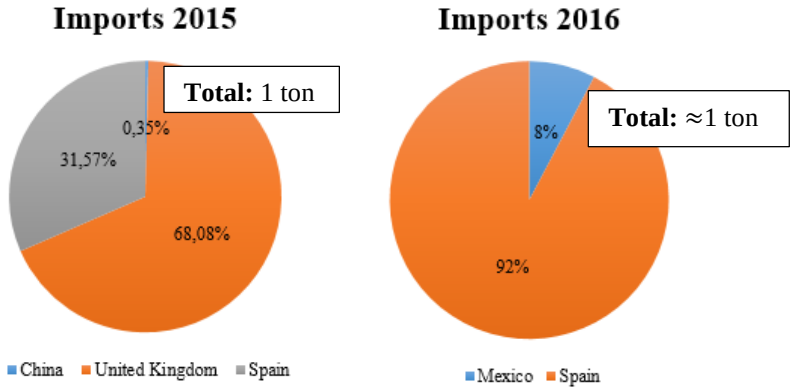
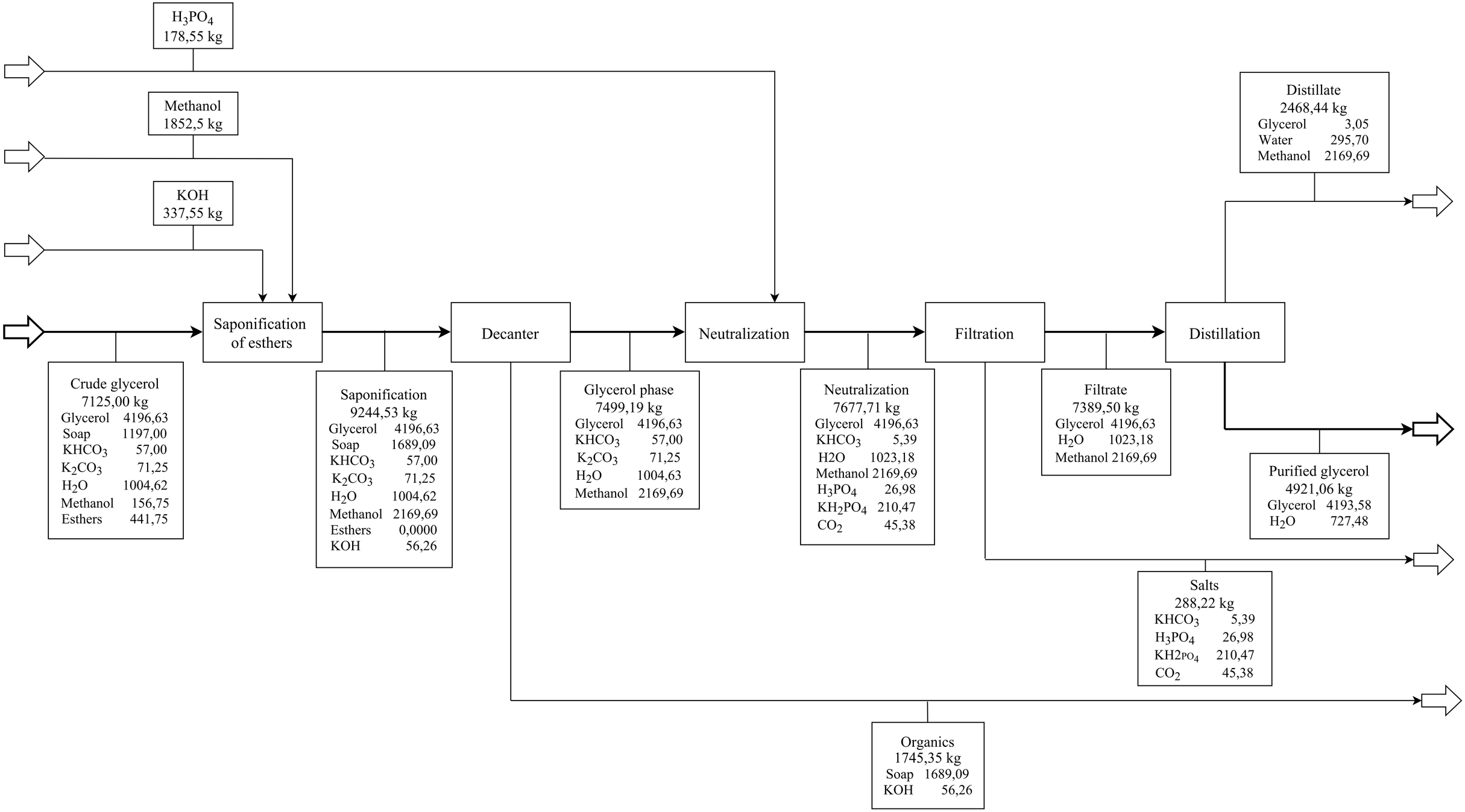


Figure A7. Reported exports of acetaldehyde

Appendix B. Process diagrams



Operation: 8000 h/year

All amounts in kg

Product "Purified Glycerol"
41948,6 ton/y
Purification of Crude Glycerol

Date: 10/2016

(Drawing No. 4)

Water_in
411,80 Kg/h

Absorption Column

Non-condensable gases
2093,02 Kg/h

Acrolein	86,51
Acetaldehyde	62,12
H2	17,95
Ethylene	836,56
H2O	9,89
CO	1079,99

Non_condensable gases_ 2
23,18 Kg/h

Acrolein	1,93
Acetaldehyde	15,83
H2	0,009
Ethylene	0,3484
CO	4,97
H2O	0,097

Liq_2
502,99 Kg/h

Acrolein	56,83
Acetaldehyde	35,56
H2	0,0012
Ethylene	0,047
H2O	409,67
CO	0,887

Gas_2
2184,20 Kg/h

Acrolein	143,34
Acetaldehyde	97,67
H2	17,95
Ethylene	836,61
H2O	7,76
CO	1080,88

Acetaldehyde
301,23 Kg/h

Acrolein	69,06
Acetaldehyde	226,33
H2	0,0005
Ethylene	0,193
CO	0,361
H2O	5,29

Gases
993,55 Kg/h

Acrolein	527,88
Acetaldehyde	284,10
H2	0,0094
H2O	115,69
Ethylene	0,54
CO	5,33

Recycle_c
570,12 Kg/h

H2O	1,91
Glycerol	568,22

Reactor

Separator 1

Distillation 2

Purified glycerol
4937,01 Kg/h

Glycerol	4706,83
Water	230,18

Reactor_out
4937,01 Kg/h

Acrolein	693,07
Acetaldehyde	392,39
H2	17,96
Ethylene	837,10
H2O	1911,17
CO	1085,32

Distillation 1

Heavy
7,57 Kg/h

Acrolein	4,80
Acetaldehyde	0,27
H2O	2,50
Glycerol	0,0039

Liq_1
2752,81 Kg/h

Acrolein	549,74
Acetaldehyde	294,72
H2	0,0082
Ethylene	0,49
H2O	1903,41
CO	4,44

Liq_3
609,22 Kg/h

Acrolein	456,94
Acetaldehyde	41,97
H2O	110,30

Glycerol
0,77 Kg/h

R+Glycerol
570,90 Kg/h

H2O	1,91
Glycerol	568,99

Acrolein
498,61 Kg/h

Acrolein	452,12
Acetaldehyde	41,70
H2O	4,02
Glycerol	0,77

Distillation 3

Water
673,91 Kg/h

H2O	105,69
Glycerol	568,22

Water_out
103,79 kg/h

Distillation 4

Gly_out
570,12 Kg/h

H2O	1,91
Glycerol	568,22

Water_2
2322,25 Kg/h

Acrolein	78,68
Acetaldehyde	46,18
H2O	2197,39

Operation: 8000 h/year

All Flows in Kg/h

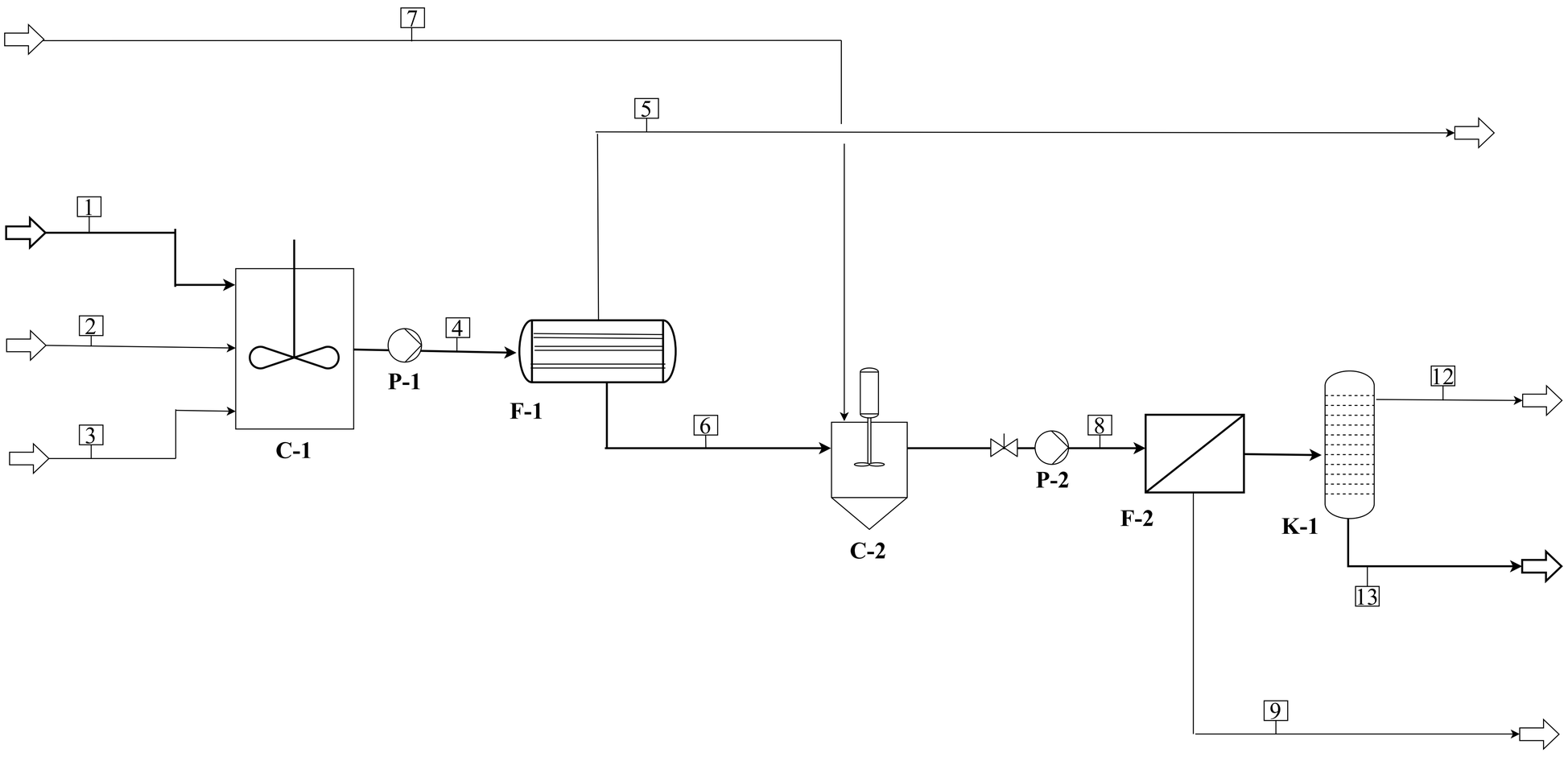
Product "Acrolein" 3988,84 ton/yr
Dehydration
Block Diagram

Date: 10/2016

(Drawing No. 4)

Process recipe:

Raw glycerol was fed into reactor at 25 °C and solid potassium hydroxide is dissolved in methanol and addedunder stirring to the reactor to start saponification of the esters. The reaction mixture continues to a decanter where potassium hydroxide and soaps are separated from glycerol at standardconditions (25°C, 1 bar). After 60 min, the mixture is neutralized with concentrated phosphoric acid and the mixture is stirred for 15 min.Precipitated salts are removed by filtration and the excess methanol is distilled in K-1 at 25°C and 1,01 bar over a 50 min period. Then the glycerol obtained is cooled to 30°C.



Identification number	Denomination	Identification number	Denomination
C-1	Saponification reactor	**F-2**	Filter
F-1	Decanter	**K-2**	Distillation column
C-2	Neutralization reactor		

Operation: 8000 h / year

Pure Glycerol Production 41948,6 ton/y

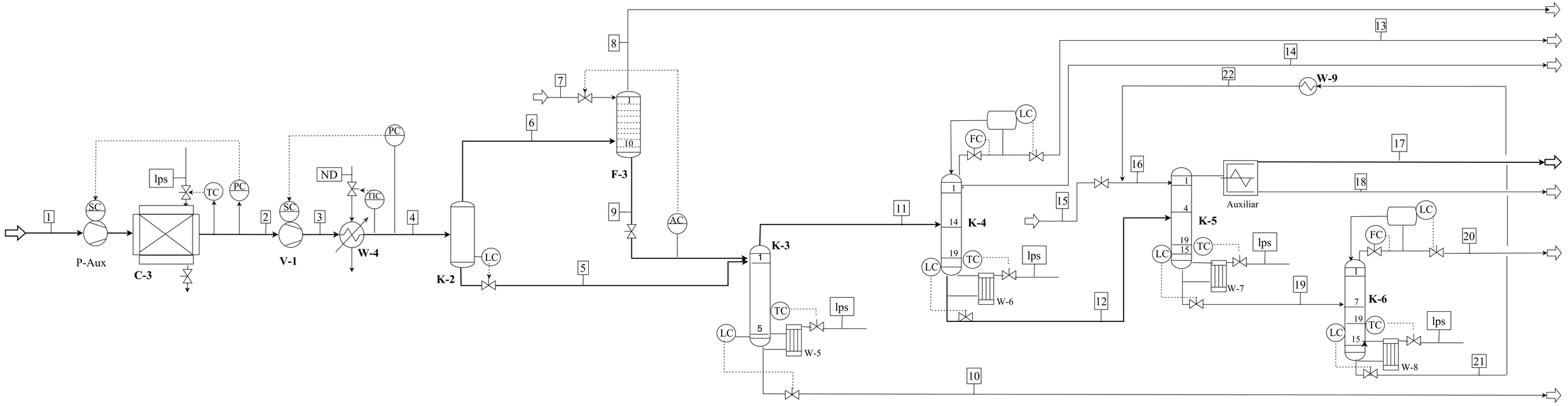
Purification Process

Process Flow Diagram

Designer: Andrea Castañeda

Date 11/2016 Drawing No. 4

Flow No.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Product		Purified Glycerol	Reactor_out	Gas_1p	Gas_1c	Liq_1	Gas_2	Water_in	Non-condensable gases	Liq_2	Water 2	Gases	Liq_3_2	Acetaldehyde	Non-condensable gases_2	Glycerol	R+Glycerol	Acrolein	Heavy	Water	Water_out	Gly_out	Recycle_c
Acrolein	Kg/h		693,07	693,07	693,07	549,74	143,34		86,51	56,83	78,68	527,88	456,92	69,06	1,93			452,12	4,80				
Acetaldehyde	Kg/h		392,39	392,39	392,39	294,72	97,67		62,12	35,56	46,18	284,10	41,98	226,33	15,83			41,70	0,2741				
Hydrogen	Kg/h		17,96	17,96	17,96	0,0082	17,95		17,95	0,0012		0,0094		0,0005	0,0090								
Water	Kg/h	230,18	1911,17	1911,21	1911,21	1903,41	7,76	411,80	9,89	409,67	2197,39	115,69	110,30	5,29	0,097		1,91	4,02	2,50	105,68	130,79	1,91	1,91
Glycerol	Kg/h	4706,83														0,77	568,99	0,77	0,0039	568,22		568,22	568,22
Ethyelene	Kg/h		837,10	837,10	837,10	0,495	836,61		836,56	0,047		0,54		0,193	0,35								
Carbon monoxide	Kg/h		1085,32	1085,32	1085,32	4,44	1080,88		1079,99	0,89		5,33		0,361	4,97								
Flow rate	Kg/h	4937,02	4937,01	4937,01	4937,01	2752,81	2184,20	411,80	2093,02	502,99	2322,17	993,55	609,19	301,23	23,17	0,77	570,99	498,61	7,57	673,91	130,79	570,13	
Operating pressure	bar	2,01	2,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	11,01	10,00
Operating temperature	°C	410,00	153,60	371,00	34,40	34,40	34,40	20,00	38,69	38,69	172,30	137,90	138,30	90,00	90,00	80,00	80,00	30,00	30,00	228,90	184,10	383,00	80,00
Density	Kg/m^3	2,77	1,38	5,00	26,05	943,10	11,70	1011,00	11,25	964,00	869,78	15,22	718,42	693,90	15,62	1172,44	1172,44	823,37	886,62	730,02	870,48	638,75	1172,00



Identification number	Denomination	Identification number	Denomination	Identification number	Denomination	Identification number	Denomination	Identification number	Denomination
C-3	Packed bed reactor	**W-4**	Fixed tube heat exchanger	**F-3**	Absorption column	**K-4**	Distillation column	**K-6**	Distillation column
V-1	Centrifugal compresor	**K-2**	Flash separator	**K-3**	Distillation column	**K-5**	Distillation column	**W-9**	Cooler

Operation: 8000 h / year

Acrolein Production 3988,84 ton/y

Dehydration process

Process Flow Diagram

Designer: Andrea Castañeda

Date 11/2016 Drawing No. 5

Appendix C. Specification data sheets

Base case

- **Glycerol purification process**

Table C1. Specification data sheet for saponification reactor (C-1)

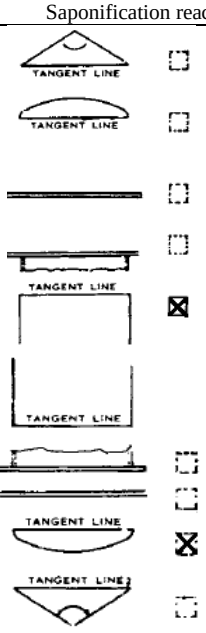
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
C-1		Saponification reactor was defined as a vertical vessel		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Glycerol, soap, esters, methanol, water,			Type	
potasium carbonate, potasium bicarbonate			Blind flange cover	
PRESSURE:			Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	1,6 m
TEST:			LENGTH:	4,8 m
TEMPERATURE:				
DESIGN:	25°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	Saponification of esters to remove it from crude glycerol	
Non-jacketed separator		LOCATION	External	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C2. Specification data sheet for decanter (F-1)

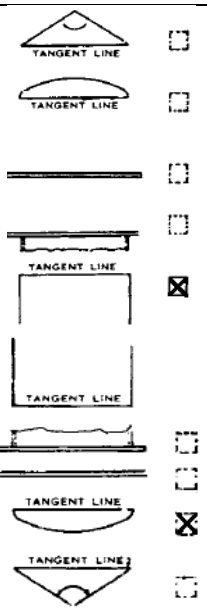
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
F-1		Decanter was defined as a vertical vessel		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Glycerol, soap, esters, methanol, water,			Type	
potasium carbonate, potasium bicarbonate			Blind flange cover	
PRESSURE:			Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	1,199 m
TEST:			LENGTH:	3,60 m
TEMPERATURE:				
DESIGN:	25°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	Separation of the organic and glycerol phases resulting to the saponification process	
Non-jacketed separator		LOCATION	External	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C3. Specification data sheet for neutralization reactor (C-2)

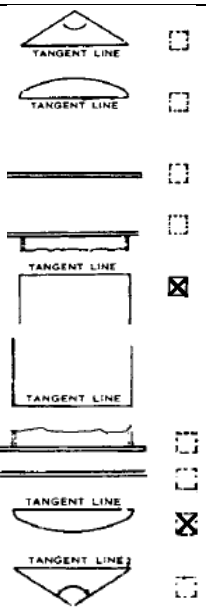
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
C-2		Neutralization reactor was defined as a vertical vessel		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Glycerol, soap, esters, methanol, water,			Type	
potasium carbonate, potasium bicarbonate			Blind flange cover	
PRESSURE:			Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	2,11 m
TEST:			LENGTH:	6,63 m
TEMPERATURE:				
DESIGN:	25°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	Neutralization of salts to remove it from crude glycerol	
Non-jacketed separator		LOCATION	External	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C4. Specification data sheet for filter (F-2)

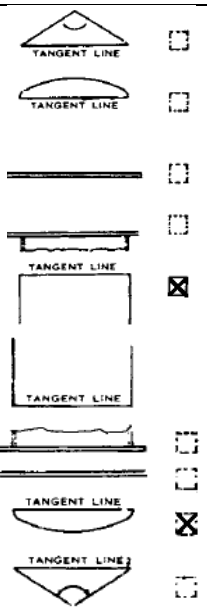
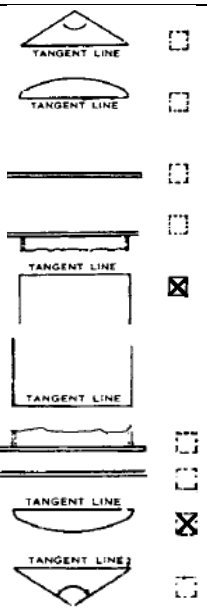
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
F-2		Decanter was defined as a vertical vessel		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Glycerol, soap, esters, methanol, water, potasium bicarbonate, phosphoric acid, potassium phosphate, carbon dioxide			Type	
			Blind flange cover	
PRESSURE:			Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,71 m
TEST:			LENGTH:	2,13 m
TEMPERATURE:				
DESIGN:	25°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	The filter was used to separate the salts from crude glycerol	
Non-jacketed separator		LOCATION	External	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C5. Specification data sheet for distillation column (K-1)

COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-1		Distillation column		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Glycerol, water and methanol			Type	
			Blind flange cover	
PRESSURE:			Flang top closure	
OPERATING:			Straight Shell	
DESIGN:	10 bar		DIAMETER (O.D):	0,60 m
TEST:			LENGTH:	5,48 m
TEMPERATURE:				
DESIGN:	250°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	The distillation column separates the methanol solution from the glycerol	
Jacketed column disitillation		LOCATION	External	
Material of protection	Paint		Date: 2015 Revisions: 2016	

- **Acrolein purification process**

Table C6. Specification data sheet for packed bed reactor (C-3)

STANDARDS OF TUBULAR EXCHANGER MANUFACTURERS ASSOCIATION
EXCHANGER SPECIFICATION SHEET

CUSTOMER: Acrolein production plant		JOB NO.
		REFERENCE NO. C-3
ADRESS		INQUIRY NO. 1
PLANT LOCATION: Santa Marta		DATE: 11/2015
SERVICE OF UNIT		ITEM NO. 1
SIZE	TYPE: Fixed tube	CONNECTED IN
GROSS SURFACE PR UNIT	SHELLS PER UNIT	SURFACE PER SHELL
PERFORMANCE OF ONE UNIT		
	SHELL SIDE	TUBE SIDE
FLUID CIRCULATE	Steam low pressure	Glycerol
TOTAL FLUID ENTERING (Kmol/h)	269,3019	4706,8311
VAPOR (Kmol/h)		
LIQUID (Kmol/h)		4706,8311
STEAM (Kmol/h)	269,3019	
SPECIFIC HEAT-LIQUIDS	971 BTU/LB/°F	0,424 BTU/LB/°F
LATENT HEAT-VAPORS	BTU/LB/°F	BTU/LB/°F
TEMPERATURE IN	290,48 °F	770 °F
TEMPERATURE OUT	308,48 °F	308,4 °F
OPERATING PRESSURE	PSI	PSI
NUMBER OF PASES PER SHELL	1	1
VELOCITY	FT/SEC	FT/SEC
PRESSURE DROP		
FOULING RESISTANCE		
HEAT EXCHANGED-BTU/HR	M.T.D (Corrected)	
TRANSFER RATE-SERVICE	EFF SURFACE PER UNIT	

CONSTRUCTION

DESIGN PRESSURE		29,2 PSI		PSI
TEST PRESSURE		PSI		PSI
DESIGN TEMPERATURE		°F		°F
TUBES	NO. 36688	O.D. 0,75” BWG	LENGTH 16’	PITCH 1”
SHELL		I.D. O.D. 3”		
SHELL COVER: Austenitic Stainless Stell			FLOATING HAD COVER: Austenitic Stainless Stell	
CORROSION ALLOWANCE-SHELL SIDE	0,04 in		TUBE SIDE 0,04 in	
CODE REQUIREMENTS			TEMA CLASS	

Table C7. Specification data sheet for compressor (V-1)

CENTRIFUGAL COMPRESSOR				SHEET NO.	REV
SPECIFICATION				DATE: 2015	
				BY: Andrea Castañeda	CHKD
ITEM NO. V-1	SERVICE			JOB NO.	
NO. REQ'D	DRIVE	MANUFACTURE			
GAS HANDLED				SIZE & TYPE	STAGES: 1
CORROSION FACTORS				DESCRIPTION	
OPERATING CONDITION	1	2	3	COMPRESSORS MATERIALS	
CAPACITY	2110 gpm			CASE:Austenitic Stainless Steel	
CFM@ INLET CONDS				DIAPHRAGMS	
WT. FLOW. LBS/HR.	10884			GUIDE VANES	
(M'SCFD) (SCFM)	2929 gpm			INTER SATGE LABYRINTHS	
TEMP. INLET. °F	308,462			IMPELLER HUBS&COVERS	
DISCH. °F	78,998			IMPLLER VANES	
PRESS. INLET. PSIA	29,196			SHAFT	
DISCH. PSIA	159,686			SHAFT SLEEVES	
DIFFER. PSI	130,49			BALANCE DRUM OR DISC	
COMP. RATIO	79,33			CONSTRUCTION DETAILS	
MOLECULAR WT.				CASE: SWP	PSIG. MAX. HYDTEST PSIG 10 bar
SP. GR. (AIR)				SPLIT: HORIZONTAL	
REL. HUMIDITY, %				SUPPORT: FOOT	
"K" VALUE. CP/CV	1,264			IMPLELLER: TYPE: ENCLOSED	
COMPRESSIBILITY, "Z"				CONSTR: WELDED	
ELEV. ABOVE SEA LEVEL	20 ft			DIAMETER	"VANE SHICKNESS"
BHP (NCL. GEAR LOSS)				SHAFT: DIAM. AT IMP	"AT BRGS"
RPM				SPAN: C.C BRGS	"IMP OVERMANG"
IMP TIP VEL. FPD				CRITICAL SPEED	
WATER RATE. #/HP/HR				BRGS: LOCATION (INTERNAL: EXTERNAL)	
				RADIAL: TYPE	PROJ. AREA SQ"
MAX. CO. CFM@INL 2109		MAX. BHP		THRUST: TYPE	EFF. AREA SQ"
MIN. CFM. (SURGE POINT)				SEALS:	
CONTROL SPEED: SUCTION VALVE					
SOURCE MANUAL: PC				COUPLING	CPLG GRD: YES. NO
STEAM: PRESS	PSIG: TEMP		°F:EXH	BASE PLATE:	
POWER 900 HP	VOLTS: PH.	CYC. COOLING WATER	°F		

Table C8. Specification data sheet for fixed tube heat exchanger or cooler (W-4)

STANDARDS OF TUBULAR EXCHANGER MANUFACTURERS ASSOCIATION

EXCHANGER SPECIFICATION SHEET

CUSTOMER: Acrolein production plant		JOB NO.
		REFERENCE NO. W-4
ADRESS		INQUIRY NO.
PLANT LOCATION: Santa Marta		DATE: 11/2015
SERVICE OF UNIT		ITEM NO.
SIZE	TYPE: Fixed tube	CONNECTED IN
GROSS SURFACE PR UNIT	SHELLS PER UNIT	SURFACE PER SHELL
PERFORMANCE OF ONE UNIT		
	SHELL SIDE	TUBE SIDE
FLUID CIRCULATE	Cooling water	Gas 1-P
TOTAL FLUID ENTERING (Kmol/h)		204,85
VAPOR (Kmol/h)		
LIQUID (Kmol/h)	4,4780	
STEAM (Kmol/h)		
SPECIFIC HEAT-LIQUIDS	972 BTU/LB/°F	BTU/LB/°F
LATENT HEAT-VAPORS	BTU/LB/°F	BTU/LB/°F
TEMPERATURE IN	75,92 °F	699,8 °F
TEMPERATURE OUT	93,91 °F	93,8 °F
OPERATING PRESSURE	PSI	PSI
NUMBER OF PASES PER SHELL	1	1
VELOCITY	FT/SEC	FT/SEC
PRESSURE DROP		
FOULING RESISTANCE		
HEAT EXCHANGED-BTU/HR	M.T.D (Corrected)	
TRANSFER RATE-SERVICE	EFF SURFACE PER UNIT	

CONSTRUCTION

DESIGN PRESSURE	160 PSI				PSI
TEST PRESSURE	PSI				PSI
DESIGN TEMPERATURE	°F				°F
TUBES NO.	O.D. 0,75”	BWG	LENGTH 16’	PITCH 1”	
SHELL	I.D.	O.D. 3’			
SHELL COVER: Austenitic Stainless Stell			FLOATING HAD COVER: Austenitic Stainless Stell		
CORROSION ALLOWANCE-SHELL SIDE 0,04 in			TUBE SIDE 0,04 in		

Table C9. Specification data sheet for flash separator (K-2)

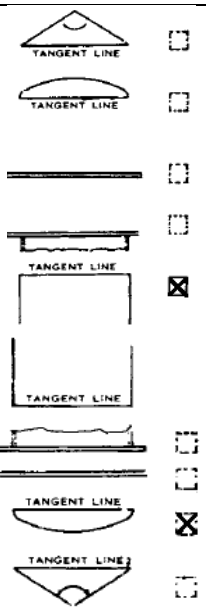
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-2		Flash separator K-2		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, hydrogen, Ethylene, water, carbon monoxide			Type	
			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,39 m
TEST:			LENGTH:	1,96 m
TEMPERATURE:				
DESIGN:	34,4°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	It is used to separate the non-condensable gases	
Jacketed flash separator		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C10. Specification data sheet for absorption column (F-3)

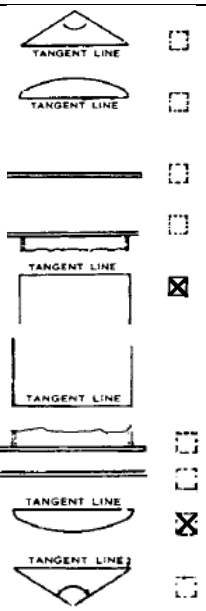
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
F-3		Absorption column F-3		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, hydrogen			Type	
Ethylene, water, carbon monoxide			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,57 m
TEST:			LENGTH:	4,8 m
TEMPERATURE:				
DESIGN:	37°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	To eliminate non-condensable gases (H_2, CO, ethylene)	
Jacketed absorption column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C11. Specification data sheet for distillation column (K-3)

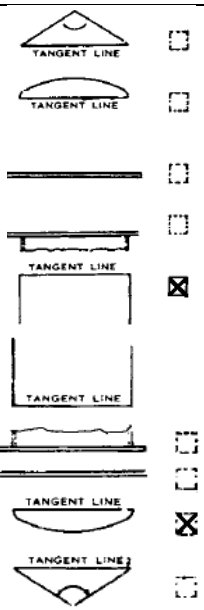
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-3		Distillation column K-3		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, hydrogen			Type	
Ethylene, water, carbon monoxide			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,75 m
TEST:			LENGTH:	9,94 m
TEMPERATURE:				
DESIGN:	172,3°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	To eliminate water	
Jacketed distillation column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C12. Specification data sheet for distillation column (K-4)

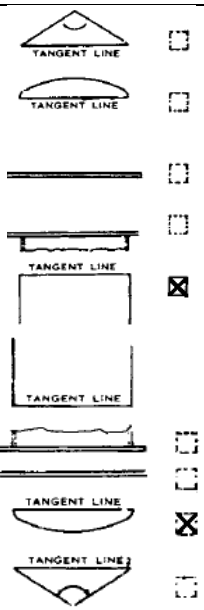
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-4		Distillation column K-4		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, water			Type	
			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,77 m
TEST:			LENGTH:	10,96 m
TEMPERATURE:				
DESIGN:	183,3°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	It is used to separate acetaldehyde from the acrolein and other compounds	
Jacketed distillation column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C13. Specification data sheet for azeotropic distillation column (K-5)

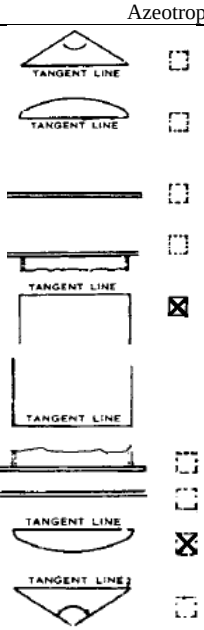
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-5		Azeotropic distillation column K-5		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, water			Type	
			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,25 m
TEST:			LENGTH:	8,46 m
TEMPERATURE:				
DESIGN:	228,9°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	It is used to separate to separate the acrolein from other compounds	
Jacketed distillation column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C14. Specification data sheet for distillation column (K-6)

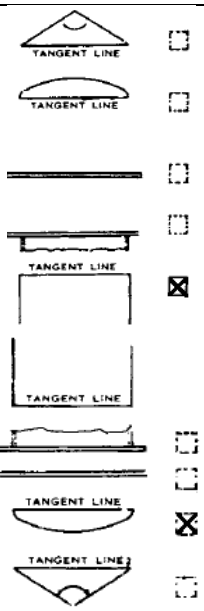
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-6		Distillation column K-6		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Glycerol, water			Type	
			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,91 m
TEST:			LENGTH:	5,6 m
TEMPERATURE:				
DESIGN:	383°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	To purify glycerol and recycle it to K-5	
Jacketed distillation column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C15. Specification data sheet for fixed tube heat exchanger or cooler (W-9)

STANDARDS OF TUBULAR EXCHANGER MANUFACTURERS ASSOCIATION

EXCHANGER SPECIFICATION SHEET

CUSTOMER: Acrolein production plant		JOB NO.
		REFERENCE NO. W-9
ADRESS		INQUIRY NO.
PLANT LOCATION: Santa Marta		DATE: 11/2015
SERVICE OF UNIT		ITEM NO.
SIZE	TYPE: Fixed tube	CONNECTED IN
GROSS SURFACE PR UNIT	SHELLS PER UNIT	SURFACE PER SHELL
PERFORMANCE OF ONE UNIT		
	SHELL SIDE	TUBE SIDE
FLUID CIRCULATE	Cooling water	Glycerol-out
TOTAL FLUID ENTERING (Kmol/h)	1,3265	6,2757
VAPOR (Kmol/h)		
LIQUID (Kmol/h)	1,3265	6,2757
STEAM (Kmol/h)		
SPECIFIC HEAT-LIQUIDS	972 BTU/LB/°F	1,37 BTU/LB/°F
LATENT HEAT-VAPORS	BTU/LB/°F	BTU/LB/°F
TEMPERATURE IN	89,33 °F	721,44 °F
TEMPERATURE OUT	107,33 °F	176 °F
OPERATING PRESSURE	PSI	PSI
NUMBER OF PASES PER SHELL	1	1
VELOCITY	FT/SEC	FT/SEC
PRESSURE DROP		
FOULING RESISTANCE		
HEAT EXCHANGED-BTU/HR	M.T.D (Corrected)	
TRANSFER RATE-SERVICE	EFF SURFACE PER UNIT	

CONSTRUCTION

DESIGN PRESSURE		160 PSI		PSI
TEST PRESSURE		PSI		PSI
DESIGN TEMPERATURE		°F		°F
TUBES NO. 36688	O.D. 0,75” BWG		LENGTH 26’ PITCH	
SHELL	I.D. 1’ O.D.			
SHELL COVER			FLOATING HAD COVER	
CORROSION ALLOWANCE-SHELL SIDE	0,04 in		TUBE SIDE 0,04 in	

Optimized case

- **Acrolein purification process**

Table C16. Specification data sheet for packed bed reactor (C-3)

STANDARDS OF TUBULAR EXCHANGER MANUFACTURERS ASSOCIATION

EXCHANGER SPECIFICATION SHEET

CUSTOMER: Acrolein production plant		JOB NO.
		REFERENCE NO. C-3
ADRESS		INQUIRY NO. 1
PLANT LOCATION: Santa Marta		DATE: 11/2015
SERVICE OF UNIT		ITEM NO. 1
SIZE	TYPE: Fixed tube	CONNECTED IN
GROSS SURFACE PR UNIT	SHELLS PER UNIT	SURFACE PER SHELL
PERFORMANCE OF ONE UNIT		
	SHELL SIDE	TUBE SIDE
FLUID CIRCULATE	Steam low pressure	Glycerol
TOTAL FLUID ENTERING (Kmol/h)	240,2292	4706,8311
VAPOR (Kmol/h)		
LIQUID (Kmol/h)		4706,8311
STEAM (Kmol/h)	240,2292	
SPECIFIC HEAT-LIQUIDS	971 BTU/LB/°F	0,424 BTU/LB/°F
LATENT HEAT-VAPORS	BTU/LB/°F	BTU/LB/°F
TEMPERATURE IN	290,48 °F	770 °F
TEMPERATURE OUT	308,48 °F	358,32 °F
OPERATING PRESSURE	PSI	PSI
NUMBER OF PASES PER SHELL	1	1
VELOCITY	FT/SEC	FT/SEC
PRESSURE DROP		
FOULING RESISTANCE		
HEAT EXCHANGED-BTU/HR	M.T.D (Corrected)	
TRANSFER RATE-SERVICE	EFF SURFACE PER UNIT	

CONSTRUCTION

DESIGN PRESSURE	29,2 PSI			PSI
TEST PRESSURE	PSI			PSI
DESIGN TEMPERATURE	°F			°F
TUBES NO. 36688	O.D. 0,75" BWG		LENGTH 16'	PITCH 1"
SHELL	I.D.	O.D.		
SHELL COVER: Austenitic Stainless Stell			FLOATING HAD COVER: Austenitic Stainless Stell	
CORROSION ALLOWANCE-SHELL SIDE	0,04 in		TUBE SIDE 0,04 in	
CODE REQUIREMENTS			TEMA CLASS	

Table C17. Specification data sheet for compressor (V-1)

CENTRIFUGAL COMPRESSOR SPECIFICATION				SHEET NO. REV DATE: 2015 BY: Andrea Castañeda CHKD
ITEM NO. V-1	SERVICE			JOB NO.
NO. REQ'D	DRIVE	MANUFACTURE		
GAS HANDLED				SIZE & TYPE STAGES: 1
CORROSION FACTORS				DESCRIPTION
OPERATING CONDITION	1	2	3	COMPRESSORS MATERIALS
CAPACITY	2042,30 gpm			CASE: Austenitic Stainless Steel
CFM@ INLET CONDS				DIAPHRAGMS
WT. FLOW. LBS/HR.	10884			GUIDE VANES
(M'SCFD) (SCFM)	2835,76 gpm			INTER SATGE LABYRINTHS
TEMP. INLET. °F	308,48			IMPELLER HUBS&COVERS
DISCH. °F	100			IMPLLER VANES
PRESS. INLET. PSIA	29,196			SHAFT
DISCH. PSIA	159,686			SHAFT SLEEVES
DIFFER. PSI	130,49			BALANCE DRUM OR DISC
COMP. RATIO	79,33			CONSTRUCTION DETAILS
MOLECULAR WT.				CASE: SWP PSIG. MAX. HYDTEST PSIG 10 bar
SP. GR. (AIR)				SPLIT: HORIZONTAL
REL. HUMIDITY, %				SUPPORT: FOOT
"K" VALUE. CP/CV	1,229			IMPLELLER: TYPE: ENCLOSED
COMPRESSIBILITY, "Z"				CONSTR: WELDED
ELEV. ABOVE SEA LEVEL	20 ft			DIAMETER "VANE SHICKNESS"
BHP (NCL. GEAR LOSS)				SHAFT: DIAM. AT IMP "AT BRGS"
RPM				SPAN: C.C BRGS "IMP OVERMANG"
IMP TIP VEL. FPD				CRITICAL SPEED
WATER RATE. #/HP/HR				BRGS: LOCATION (INTERNAL: EXTERNAL)
				RADIAL: TYPE PROJ. AREA SQ"
MAX. CO. CFM@INL 2042		MAX. BHP		THRUST: TYPE EFF. AREA SQ"
MIN. CFM. (SURGE POINT)				SEALS:
CONTROL (SPEED: SUCTION VALVE, INLET VANES)				
SOURCE: (MANUAL: PC: PC: TC)				COUPLING CPLG GRD: YES. NO
STEAM: PRESS	PSIG: TEMP		°F:EXH	BASE PLATE:
POWER 900 HP	VOLTS: PH.	CYC. COOLING WATER	°F	

Table C18. Specification data sheet for fixed tube heat exchanger or cooler (W-4)

STANDARDS OF TUBULAR EXCHANGER MANUFACTURERS ASSOCIATION

EXCHANGER SPECIFICATION SHEET

CUSTOMER: Acrolein production plant		JOB NO.
		REFERENCE NO. W-4
ADRESS		INQUIRY NO.
PLANT LOCATION: Santa Marta		DATE: 11/2015
SERVICE OF UNIT		ITEM NO.
SIZE	TYPE: Fixed tube	CONNECTED IN
GROSS SURFACE PR UNIT	SHELLS PER UNIT	SURFACE PER SHELL
PERFORMANCE OF ONE UNIT		
	SHELL SIDE	TUBE SIDE
FLUID CIRCULATE	Cooling water	Gas 1-P
TOTAL FLUID ENTERING (Kmol/h)		186,47
VAPOR (Kmol/h)		
LIQUID (Kmol/h)	4,7331	
STEAM (Kmol/h)		
SPECIFIC HEAT-LIQUIDS	972 BTU/LB/°F	BTU/LB/°F
LATENT HEAT-VAPORS	BTU/LB/°F	BTU/LB/°F
TEMPERATURE IN	75,92 °F	723,866 °F
TEMPERATURE OUT	93,91 °F	93,92 °F
OPERATING PRESSURE	PSI	PSI
NUMBER OF PASES PER SHELL	1	1
VELOCITY	FT/SEC	FT/SEC
PRESSURE DROP		
FOULING RESISTANCE		
HEAT EXCHANGED-BTU/HR	M.T.D (Corrected)	
TRANSFER RATE-SERVICE	EFF SURFACE PER UNIT	

CONSTRUCTION

DESIGN PRESSURE	160 PSI			PSI
TEST PRESSURE	PSI			PSI
DESIGN TEMPERATURE	°F			°F
TUBES NO.	O.D. 0,75”	BWG	LENGTH 16’	PITCH 1”
SHELL	I.D.	O.D. 3’		
SHELL COVER: Austenitic Stainless Stell			FLOATING HAD COVER: Austenitic Stainless Stell	
CORROSION ALLOWANCE-SHELL SIDE 0,04 in			TUBE SIDE 0,04 in	

Table C19. Specification data sheet for flash separator (K-2)

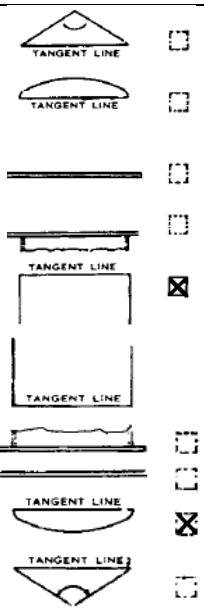
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-2		Flash separator K-2		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, hydrogen, Ethylene, water, carbon monoxide			Type	
			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,28 m
TEST:			LENGTH:	1,39 m
TEMPERATURE:				
DESIGN:	34,4°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	It is used to separate the non-condensable gases	
Jacketed flash separator		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C20. Specification data sheet for absorption column (F-3)

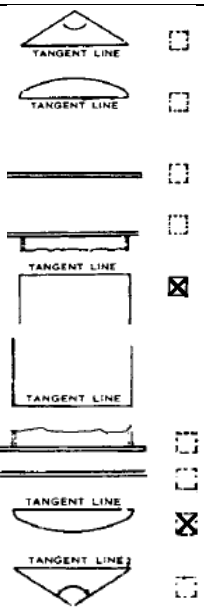
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
F-3		Absorption column F-3		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, hydrogen			Type	
Ethylene, water, carbon monoxide			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,40 m
TEST:			LENGTH:	4,8 m
TEMPERATURE:				
DESIGN:	39,2°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	To eliminate non-condensable gases (H_2, CO, ethylene)	
Jacketed absorption column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C21. Specification data sheet for distillation column (K-3)

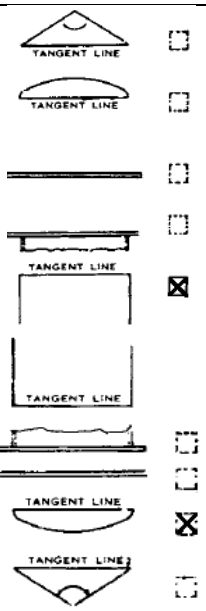
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-3		Distillation column K-3		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, hydrogen			Type	
Ethylene, water, carbon monoxide			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	1,24 m
TEST:			LENGTH:	9,95 m
TEMPERATURE:				
DESIGN:	173,1°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	To eliminate water	
Jacketed distillation column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C22. Specification data sheet for distillation column (K-4)

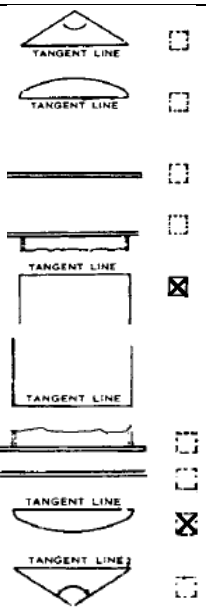
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-4		Distillation column K-4		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, water			Type	
			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	1,25 m
TEST:			LENGTH:	10,96 m
TEMPERATURE:				
DESIGN:	138,5°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	It is used to separate acetaldehyde from the acrolein and other compounds	
Jacketed distillation column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C23. Specification data sheet for azeotropic distillation column (K-5)

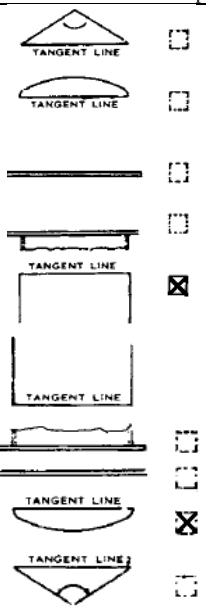
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-5		Azeotropic distillation column K-5		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Acrolein, acetaldehyde, water			Type	
			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,50 m
TEST:			LENGTH:	8,46 m
TEMPERATURE:				
DESIGN:	195°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	It is used to separate to separate the acrolein from other compounds	
Jacketed distillation column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C24. Specification data sheet for distillation column (K-6)

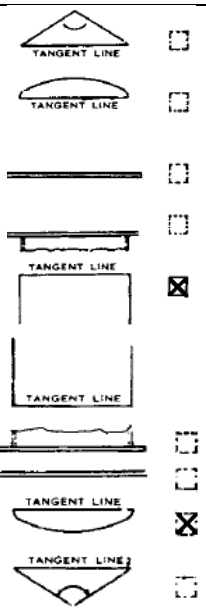
COLUMN SPECIFICATION				
ITEM NO.	NO REQ'D	DESCRIPTION		
K-6		Distillation column K-6		
PERFORMANCE DATA			Conical head	
FLUIDS PROCESSED:			Dished head	
Glycerol, water			Type	
			Blind flange cover	
PRESSURE:	11,01 bar		Flang top closure	
OPERATING:			Straight Shell	
DESIGN:			DIAMETER (O.D):	0,85 m
TEST:			LENGTH:	5,4 m
TEMPERATURE:				
DESIGN:	383°C			
TEST:				
CONSTRUCTION DATA				
MATERIAL OF CONSTRUCTION	Austenitic Stainless Steel	DESCRIPTION OF FUNCTION OF VESSEL AND	To purify glycerol and recycle it to K-5	
Jacketed distillation column		LOCATION	Internal	
Material of protection	Paint		Date: 2015 Revisions: 2016	

Table C25. Specification data sheet for fixed tube heat exchanger or cooler (W-9)

STANDARDS OF TUBULAR EXCHANGER MANUFACTURERS ASSOCIATION

EXCHANGER SPECIFICATION SHEET

CUSTOMER: Acrolein production plant		JOB NO.
		REFERENCE NO. W-9
ADRESS		INQUIRY NO.
PLANT LOCATION: Santa Marta		DATE: 11/2015
SERVICE OF UNIT		ITEM NO.
SIZE	TYPE: Fixed tube	CONNECTED IN
GROSS SURFACE PR UNIT	SHELLS PER UNIT	SURFACE PER SHELL
PERFORMANCE OF ONE UNIT		
	SHELL SIDE	TUBE SIDE
FLUID CIRCULATE	Cooling water	Glycerol-out
TOTAL FLUID ENTERING (Kmol/h)	0,0894	0,422
VAPOR (Kmol/h)		
LIQUID (Kmol/h)	0,0894	0,422
STEAM (Kmol/h)		
NON-CONDENSABLES		
FLUID VAPORIZED OR CONDENSED		
STEAM CONDENSED		
GRAVITY-LIQUID		
VISCOSITY-LIQUID		
MOLECULAR WEIGHT-VAPORS		
SPECIFIC HEAT-LIQUIDS	972 BTU/LB/°F	1,37 BTU/LB/°F
LATENT HEAT-VAPORS	BTU/LB/°F	BTU/LB/°F
TEMPERATURE IN	89,33 °F	721,4 °F
TEMPERATURE OUT	107,33 °F	176 °F
OPERATING PRESSURE	PSI	PSI
NUMBER OF PASES PER SHELL	1	1
VELOCITY	FT/SEC	FT/SEC
PRESSURE DROP		
FOULING RESISTANCE		
HEAT EXCHANGED-BTU/HR	M.T.D (Corrected)	
TRANSFER RATE-SERVICE	EFF SURFACE PER UNIT	

CONSTRUCTION

DESIGN PRESSURE	160 PSI			PSI
TEST PRESSURE	PSI			PSI
DESIGN TEMPERATURE	°F			°F
TUBES NO.	O.D. 0,75" BWG		LENGTH 16'	PITCH
SHELL	I.D. 1'	O.D.		
SHELL COVER: Austenitic Stainless Stell			FLOATING HAD COVER: Austenitic Stainless Stell	
CORROSION ALLOWANCE-SHELL SIDE	0,04 in		TUBE SIDE 0,04 in	

Appendix D. Equipment and plant costing

Base Case

Table D1. Cost of products

	Production (ton/year)	Cost (USD/ton)	Cost (USD/year)
Acrolein	3988,84	$13.650,00	$54.447.722,98
Acetaldehyde	2409,48	$1.000,00	$2.409.478,57
Crystals	2305,76	$50,00	$115.288,00

Table D2. Total cost of raw materials for the base case design

Raw material	Unit Flow	Flow	Unit cost	Cost	Cost per year (2001)	Cost per year (2015)
Crude Glycerol	ton/year	57.000,00	$/ton	$150,00	N/A	$8.550.000,00
Potassium hydroxide	ton/year	2.700,40	$/ton	$1.000,00	N/A	$2.700.400,00
Methanol	kg/year	17.387.920,00	$/kg	$0,29	$5.112.048,48	$7.430.167,34
Phosphoric acid	ton/year	1.428,48	$/ton	$700,00	N/A	$999.936,00
					Total	$19.680.503,34

Table D3. Bare module costs in 2015 for the equipment in the base case design

	Item	Cbm_{2015} (USD)
Glycerol purification	Separator (C-1)	$208.372,70
	Separator (C-2)	$445.643,49
	Separator (F-1)	$102.885,77
	Separator (F-2)	$35.932,32
	Distillation column (K-1)	$82.811,72
Glycerol dehydration	Packed bed reactor (C-3)	$48.897,88
	Compressor (V-1)	$1.709.650,81
	Cooler (W-4)	$166.848,84
	Absorber column (F-3)	$64.817,41
	Separator (K-2)	$17.138,83
	Distillation column (K-3)	$131.637,43
	Distillation column (K-4)	$148.188,27
	Azeotropic distillation column (K-5)	$88.869,18
	Azeotropic distillation column (K-6)	$74.338,15
	Cooler (W-9)	$137.626,37

Table D4. Cost of the operating labor for the base case design

Cost of the operating labor	
Nol	3,008321791
SF	0,913242009
Work hours/year	8000
Shifts/year	1000
Shifts/operator year	300
Factor P.	3,333333333
Operators	10,0277393
Operators (rounded)	11
C_{OL} (USD/year)	$550.000,00

Table D5. Utility costs calculation data for the base case design

	Utility	**Unit utility comsuption**	**Utility consumption per year**	**Unit Cost utility**	**Cost utility**	**Cost utility per year (2001) $/Año**	**Cost utility per year (2015) $/Año**
V-1	Electric Distribution	kWh/year	4810107,42	$/kWh	$0,06	$288.606,45	$419.478,45
W-4	Cooling water	m3/year	644,8275984	$/1000m3	$14,80	$9,54	$13,87
W-9	Cooling water	m3/year	190,9970347	$/1000m3	$14,80	$2,83	$4,11
C-3	Steam	ton/year	38779,48062	$/ton	$27,70	$1.074,19	$1.561,30
Catalyst (MFI)	N/A	ton	25,41721	$/ton	$2.339,92	N/A	$59.474,24
F-3	Other water	kg/year	3294431,302	$/1000kg	$1,00	$3.294,43	$4.788,33
K-2	Electric Distribution	kw h/year	1039214642	$/ kw h	$0,06	$62.352,88	$90.627,53
K-3	Steam Low Pressure	kg/year	155145129,8	$/1000kg	$27,70	$4.297.520,10	$6.246.281,43
K-4	Steam Low Pressure	kg/year	140240763,3	$/1000kg	$27,70	$3.884.669,14	$5.646.218,33
	Cooling water	m3/year	241029,4691	$/1000m3	$14,80	$3.567,24	$5.184,84
K-5	Steam Low Pressure	kg/year	29207067,74	$/1000kg	$27,70	$809.035,78	$1.175.902,62
K-6	Steam Low Pressure	kg/year	178427029	$/1000kg	$27,70	$4.942.428,70	$7.183.631,47
	Cooling water	m3/year	32693,11106	$/1000m3	$14,80	$483,86	$703,27
						C_{ut} (USD/year)	$20.833.869,78

Optimized Case

Table D6. Cost of products

	Production (ton/year)	Cost (USD/ton)	Cost (USD/year)
Acrolein	11107,44	$13.650,00	$151.616.499,39
Acetaldehyde	1961,39	$1.000,00	$1.961.390,36
Crystals	2305,76	$50,00	$115.288,00

Table D7. Bare module costs in 2015 for the equipment in the optimized case design

	Item	Cbm_{2015} (USD)
Glycerol purification	Separator (C-1)	$208.372,70
	Separator (C-2)	$445.643,49
	Separator (F-1)	$102.885,77
	Separator (F-2)	$35.932,32
	Distillation column (K-1)	$82.811,72
Glycerol dehydration	Packed bed reactor (C-3)	$50.085,63
	Compressor (V-1)	$1.709.650,81
	Cooler (W-4)	$167.888,32
	Absorber column (F-3)	$56.744,30
	Separator (K-2)	$13.930,42
	Distillation column (K-3)	$223.843,87
	Distillation column (K-4)	$300.170,42
	Azeotropic distillation column (K-5)	$84.941,44
	Azeotropic distillation column (K-6)	$67.593,87
	Cooler (W-9)	$234.741,78

Table D8. Cost of the operating labor for the optimized case design

Cost of the operating labor	
Nol	3,008321791
SF	0,913242009
Work hours/year	8000
Shifts/year	1000
Shifts/operator year	300
Factor P.	3,333333333
Operators	10,0277393
Operators (rounded)	11
C_{OL} (USD/year)	$550.000,00

Table D9. Utility costs calculation data for the optimized case design

	Utility	Unit utility comsuption	Utility consumption per year	Unit Cost utility	Cost utility	Cost utility per year (2001) $/Año	Cost utility per year (2015) $/Año
V-1	Electric Distribution	kWh/year	4565080,7341	$/kWh	$0,06	$ 273.904,84	$398.110,24
W-4	Cooling water	m3/year	681,5663	$/1000m3	$14,80	$10,09	$14,66
W-9	Cooling water	m3/year	12,8664	$/1000m3	$14,80	$0,19	$0,28
C-3	Steam	ton/year	34593,0113	$/ton	$27,70	$958,23	$1.392,75
Catalyst (MFI)	N/A	ton	25,4172	$/ton	$2.339,92	N/A	$59.474,24
F-3	Other water	kg/year	3294431,3016	$/1000kg	$1,00	$3.294,43	$4.788,33
K-2	Electric Distribution	kw h/year	1063099112,3695	$/ kw h	$0,06	$63.785,945	$92.710,44
K-3	Steam Low Pressure	kg/year	232342862,1364	$/1000kg	$27,70	$6.435.897,28	$9.354.331,05
K-4	Steam Low Pressure	kg/year	287163823,2035	$/1000kg	$27,70	$7.954.437,90	$11.561.471,88
	Cooling water	m3/year	537714,9503	$/1000m3	$14,80	$7.958,18	$11.566,91
K-5	Steam Low Pressure	kg/year	77201228,0539	$/1000kg	$27,70	$2.138.474,02	$3.108.190,36
K-6	Steam Low Pressure	kg/year	118683771,6832	$/1000kg	$27,70	$3.287.540,48	$4.778.314,60
	Cooling water	m3/year	28396,6965	$/1000m3	$14,80	$420,27	$610,85
						C_{ut} (USD/year)	$29.370.976,57

Appendix E. Economic evaluation data

Base Case

Table E1. Initial data for the calculation of the cash flow statement for the base case design

Cost of Land, L	$437.343,29
Fixed capital investment	$4.087.177,82
Cost of operating labor	$550.000,00
Plant start-up	End Year 2
Revenue after start-up	$56.972.489,55
Cost of manufacturing	$54.441.308,63
Taxes	60%
Fixed capital investment with depreciation	$272,475
Depreciation	Use 10-year

Table E2. Cash flow statement for the base case plant design for the production of acrolein

End of year (k)	Investment	dk	CTM - SUM(dk)	R	COMd	(R-COM-dk)*(1-t)+dk	Cash Flow	Cumulative Cash Flow
0	($437.343,29)	$0,00	$4.087.118,00	$0,00	$0,00	$0,00	($437.343,29)	($437.343,00)
1	($4.087.117,82)	$0,00	$4.087.118,00	$0,00	$0,00	$0,00	($4.087.117,82)	($4.524.461,00)
2	($550.000,00)	$0,00	$4.087.118,00	$0,00	$0,00	$0,00	($550.000,00)	($5.074.461,00)
3	$0,00	$408.712,00	$3.678.406,00	$56.972.490,00	$54.441.309,00	$1.257.699,44	$1.257.699,44	($3.816.761,66)
4	$0,00	$408.712,00	$3.269.694,00	$56.972.490,00	$54.441.309,00	$1.257.699,44	$1.257.699,44	($2.559.062,20)
5	$0,00	$408.712,00	$2.860.982,50	$56.972.490,00	$54.441.309,00	$1.257.699,44	$1.257.699,44	($1.301.362,79)
6	$0,00	$408.712,00	$2.452.270,69	$56.972.490,00	$54.441.309,00	$1.257.699,44	$1.257.699,44	($43.663,35)
7	$0,00	$408.712,00	$2.043.558,91	$56.972.490,00	$54.441.309,00	$1.257.699,44	$1.257.699,44	$1.214.036,08
8	$0,00	$408.712,00	$1.634.847,10	$56.972.490,00	$54.441.309,00	$1.257.699,44	$1.257.699,44	$2.471.736,00
9	$0,00	$408.712,00	$1.226.135,30	$56.972.490,00	$54.441.309,00	$1.257.699,44	$1.257.699,44	$3.729.434,96
10	$0,00	$408.712,00	$817.423,60	$56.972.490,00	$54.441.309,00	$1.257.699,44	$1.257.699,44	$4.987.134,40
11	$0,00	$408.712,00	$408.711,80	$56.972.490,00	$54.441.309,00	$1.257.699,44	$1.257.699,44	$6.244.833,83
12	$987.343,29	$408.712,00	$0,00	$56.972.490,00	$54.441.309,00	$1.366.689,25	$2.354.032,53	$8.598.866,40

-Numbers in () are negative cash flows
-R=Revenue
-dk= Costs of manufacturing/Depreciation
-t=Taxes
-CTM= Fixed capital investment
-COMd= Cost of manufacturing without depreciation

Optimized Case

Table E3. Initial data for the calculation of the cash flow statement for the optimized case design

Cost of Land, L	$437.343,29
Fixed capital investment	$4.466.579,49
Cost of operating labor	$550.000,00
Plant start-up	End Year 2
Revenue after start-up	$153.693.177,75
Cost of manufacturing	$64.308.168,89
Taxes	60%
Fixed capital investment with depreciation	$297.772
Depreciation	Use 10-year

Table E4. Cash flow statement for the optimized case plant design for the production of acrolein

End of year (k)	Investment	dk	CTM - SUM(dk)	R	COMd	(R-COM-dk)*(1-t)+dk	Cash Flow	Cumulative Cash Flow
0	($437.343,29)	$0,00	$4.466.579,00	$0,00	$0,00	$0,00	($437.343,29)	($437.343,00)
1	($4.466.579,49)	$0,00	$4.466.579,00	$0,00	$0,00	$0,00	($4.466.579,49)	($4.903.923,00)
2	($550.000,00)	$0,00	$4.466.579,00	$0,00	$0,00	$0,00	($550.000,00)	($5.453.923,00)
3	$0,00	$446.658,00	$4.019.922,00	$153.693.178,00	$64.308.169,00	$36.021.998,31	$36.021.998,31	$30.568.075,54
4	$0,00	$446.658,00	$3.573.264,00	$153.693.178,00	$64.308.169,00	$36.021.998,31	$36.021.998,31	$66.590.073,90
5	$0,00	$446.658,00	$3.126.605,60	$153.693.178,00	$64.308.169,00	$36.021.998,31	$36.021.998,31	$102.612.072,16
6	$0,00	$446.658,00	$2.679.947,70	$153.693.178,00	$64.308.169,00	$36.021.998,31	$36.021.998,31	$138.634.070,48
7	$0,00	$446.658,00	$2.233.289,75	$153.693.178,00	$64.308.169,00	$36.021.998,31	$36.021.998,31	$174.656.068,79
8	$0,00	$446.658,00	$1.786.631,80	$153.693.178,00	$64.308.169,00	$36.021.998,31	$36.021.998,31	$210.678.067,00
9	$0,00	$446.658,00	$1.339.973,80	$153.693.178,00	$64.308.169,00	$36.021.998,31	$36.021.998,31	$246.700.065,42
10	$0,00	$446.658,00	$893.315,90	$153.693.178,00	$64.308.169,00	$36.021.998,31	$36.021.998,31	$282.722.063,70
11	$0,00	$446.658,00	$446.657,90	$153.693.178,00	$64.308.169,00	$36.021.998,31	$36.021.998,31	$318.744.062,05
12	$987.343,29	$446.658,00	$0,00	$153.990.950,00	$64.308.169,00	$36.141.107,10	$37.128.450,39	$355.872.512,4

-Numbers in () are negative cash flows
-R=Revenue
-dk= Costs of manufacturing/Depreciation
-t=Taxes
-CTM= Fixed capital investment
-COMd= Cost of manufacturing without depreciation

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